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A Study of Improved Strength in Paper Made From Low-Substituted Carboxymethylcellulose Pulps

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A STUDY OF IMPROVED STRENGTH IN PAPER MADE FROM LOW-SUBSTITUTED CARBOXYMETHYLCELLULOSE PULPS

A thesis submitted by

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INTRODUCTION

Cellulose derivatives, in general, are obtained by the substitution of the hydroxyl groups in the polymer. The final properties of the derivative depend considerably on the extent and uniformity of substitution, but, in the main, the nature of the substituent group determines the chemical and colloidal behavior of the derivative. Two main features distinguish cellulose reactions from those of other hydroxyl compounds of lower molecular weight:

1. The cellulose hydroxyls may not be available for reaction because the crystallinity of the cellulose hinders access of the reagent to the hydroxyl group.
2. Excessive degradation may take place, resulting in cleavage of the cellulose chains.

Almost all of the commercially important derivatives of cellulose are either ethers or esters. They have a relatively high degree of substitution (D.S.) and are degraded during the course of the reaction, resulting in loss of the fibrous structure.

Various cellulose derivatives have been prepared however, where the treatments are modified and the D.S. limited in order to preserve the fibrous structure of the cellulose. Among them the acetyl (1, 2, 3), butyryl (3), and stearoyl (3) esters, and methyl (4), carboxymethyl (CMC) (5, 6), and cyanoethyl (7, 8) ethers are of particular interest for this study. Some of the general conclusions relevant to the substituted pulps and the handsheets made from them may be summed up as follows:

Low substitution of relatively small groups (methyl, carboxymethyl, acetyl, and even butyryl to some extent) invariably results in increased strength for the substituted pulp. The phenomenon appears to be independent of the nature of the substituent group as long as it is not very large. For instance, the hydrophilic carboxyl group in carboxymethylcellulose and the hydrophobic groups in the others display similar phenomena at low degrees of substitution. A greater amount of swelling is observed in both cases and handsheets formed from the low-substituted pulps display higher strength. It seems as if the introduction of small amounts of substituent groups increases the distance between adjacent cellulose chains in the micellar system, so that on beating, a greater number of hydroxyl groups are exposed to water than would have been the case for unsubstituted cellulose fibers.

Beyond a certain degree of substitution depending on the group introduced, the "character" of the substituent group begins to influence pulp properties. Any further substitution of hydrophobic groups for instance, results in decreased swelling and impaired handsheet strength for the pulp. Even though the fibrous structure is maintained, the fibers are cut rather than hydrated on beating. Handsheets obtained from highly substituted pulps show very little strength. The strength decrease after the optimum is quite rapid, so that increasing degrees of substitution quickly reduce the handsheet strength of the pulp below that of the unsubstituted fibers.

For cellulose substituted with hydrophobic groups if, however, a compatible medium is chosen in contrast to water (i.e. acetylated fibers in acetone), a coherent sheet of excellent strength properties is obtained. For an explanation, Campbell's hypothesis on the fiber-to-fiber bonding in the presence of water may be invoked (51). For acetylated fibers in acetone, it may be assumed that layers of acetone undergo "recrystallization," resulting in an intimate union of the fiber surfaces (1, 9). The acetylated pulps in acetone are also very easy to beat. Analogous considerations may be said to govern the behavior of low-D.S. CMC pulps in water since the carboxyl group is hydrophilic. Experiments with low-D.S. CMC pulps show that sheet strength was increased considerably with the degree of substitution, and the pulps became easier to fibrillate on beating. Walecka (5) compares the action of the carboxymethyl groups in rag pulp to that of hemicelluloses in wood pulp. Increasing D.S. was found to make the pulp slimy and very hydrated, to the point where sheet formation became exceedingly difficult if not impossible.

The extent of pulp hydration and eventual solubility due to substitution is primarily determined by the nature of the substituent group. For instance, at very low degrees of substitution, where acetylated cellulose and even CMC are barely affected, sulfoethyl cellulose is completely soluble in water. The very hydrophilic and highly ionized sulfonic acid end group is probably responsible for this behavior (10).

PREPARATION OF CARBOXYMETHYLCELLULOSES AND LOW-D.S. CARBOXYMETHYLCELLULOSE PULPS

Sodium carboxymethylcellulose (CMC) is prepared by the action of chloroacetic acid (or its sodium salt) on alkali cellulose according to the reaction

$$\text{Cell-ONa} + \text{ClCH}_2\text{COOH} \xrightarrow[(\text{NaOH})]{} \text{Cell-O-CH}_2\text{COONa}$$

Some of the chloroacetic acid is also converted to glycolic acid by the alkali. In general, the etherification of cellulose consists of the preparation of alkali cellulose with a concentrated base and the subsequent reaction of the alkali cellulose with the etherifying agent. A uniform penetration of sodium hydroxide, the swelling agent, throughout the cellulose is one of the most important factors in the reaction. The swelling agent must provide alkalinity at every point in the cellulose throughout the reaction; uniform swelling of the cellulose aids the diffusion of the etherifying reagent, chloroacetic acid, to the reaction center. The solvating agent, usually water, acts as the solvent and carrier for the sodium hydroxide and as a diluent for the etherifying agent. There is almost no etherification in the absence of water (11). The above considerations apply for the preparation of soluble CMC.

Uniformity of substitution usually improves the solubility of cellulose derivatives. Walecka (5), in preparing low-D.S. CMC pulps suitable

for papermaking, found it necessary to introduce the following modifications to the conventional carboxymethylation:

1. The reaction is carried out in a nonaqueous, "nonswelling" medium (isopropanol-methanol 7:1).

2. The accessibility of the cellulose is enhanced prior to the reaction, by solvent-exchanging the water in the fibers with methanol-benzene.

3. The concentration of alkali during the reaction is kept quite low in order to prevent mercerization of the fibers, 0.3% NaOH compared to 30-40% NaOH required for preparing alkali cellulose in conventional etherification.

The cellulose is first steeped in an isopropanol solution of chloroacetic acid and then allowed to react with boiling alkali in isopropanol-methanol solution under continuous agitation for one hour. The low-D.S. pulp thus obtained is thoroughly washed with water, freed of excess alkali by neutralization with dilute acetic acid, and then soaked in sodium bicarbonate solution in order to obtain the sodium salt form of the CMC.

It appears surprising that anything more than a surface carboxymethylation reaction is possible under the modifications outlined above. The swelling value of cellulose in isopropanol is found to be very low in comparison to that in water (12). In accordance with the generally accepted criteria for cellulose reaction, this low swelling of cellulose in the reaction medium should definitely restrict the extent of etherification to the immediately accessible surface. Moreover, the concentration of alkali (0.3% sodium hydroxide) used in the reaction seems rather low for any

appreciable cellulose etherification to be possible. Walecka (5) however claims substantial reaction penetration in the fibers of the low-D.S. CMC pulps obtained as above.

One explanation for the surprising results may lie in the possible effects of small amounts of water undoubtedly associated with the "non-aqueous" system. Even keeping in mind the enhanced accessibility of the cellulose due to prior solvent exchange, it has been shown that there is almost no etherification in the absence of water (11). Reeves and Thompson (13), found the chemical accessibility for etherification, to be 0.4% for bonedry raw cotton fibers and 0.8% for bonedry mercerized cotton fibers. When the moisture content of the fibers was raised to 6%, however, the accessibility was increased to 9.5 and 23.3%, respectively. It is found that air-dried, solvent exchanged fibers as used by Walecka (5), show a loss in weight of 6-8% on ovendrying. This is just one possible source of water. Undoubtedly the other reagents also have appreciable amounts of moisture associated with them.

A suggested mechanism may be provided, by analogy from the work of Valley (14), who found that the degradation of cellulose in alcoholic media is actually initiated by the small amounts of water in the system. It was also suggested that the accelerated rates of degradation found in acidified organic liquids are caused by a sorption of acid from the non-aqueous phase by the cellulose, so that effective acidity at the cellulose-liquid interphase is much higher than that measured in the liquid phase.

The degradation with 0.05N hydrochloric acid in butanol was found to be much higher than in water and approached the action of almost 2.0N hydrochloric acid in water.

PROPERTIES OF CARBOXYMETHYCELLULOSES AND LOW-D.S. CARBOXYMETHYLCELLULOSE PULPS

The well-known and wide variety of industrial uses of carboxymethylcellulose (CMC) have made it one of the most investigated derivatives of cellulose. Commercial CMC is used in various degrees of purity and with degrees of substitution varying from 0.3 to 1.5. The product is generally degraded and nonfibrous, and is usually sold in the water-soluble sodium salt form. Depending on the uniformity of substitution, sodium CMC begins to dissolve in water at D.S. approximately 0.4. Sodium carboxymethylcellulose thickens water solutions without precipitation over a pH range of 4 to 12, and does not gel from water solutions upon heating. In solution it acts as a protective colloid. It is not precipitated from solution by dilute solutions of salts of alkali or alkaline earth metals; it is precipitated from solution by strong acids, by salts of amphoteric multivalent metals, and by salts of heavy metals.

The dissociation constant of the polyelectrolyte is calculated to be approximately 5.0×10^{-5}, indicating that it is a moderately strong acid (15). Also, when the sodium salt is treated with mineral acid, precipitation of the CMC occurs over a wide range, commencing at pH 6.0 and not being complete until about pH 2.5 or lower. The free acid form, when obtained by acidi-

fication, is soluble only in aqueous alkali. A water dispersion of the free acid form, however, can be obtained if the conversion is accomplished by means of ion-exchange resins. The heavy metal salts of CMC are also soluble only in aqueous alkali (11).

Sodium carboxymethylcellulose can be dispersed as a swollen gel in efficiently agitated water, and in aqueous ethanol or aqueous acetone containing over 60% water. Solution clarity is found to improve by passing the solution through a colloid mill or a homogenizer. Solutions of sodium CMC are thixotropic and their viscosities depend upon the rate of shear and other variables. Viscosity studies show that there is an appreciable change in viscosity with changing pH (16). The viscosity-pH curve is not reversible if pH adjustment is made with acid or alkali. However, the acid to alkali curve (addition of sodium hydroxide to acidic solutions) can be retraced if the pH is again brought down by dialysis. The presence of electrolytes is held responsible for this behavior (16). The effects of various electrolytes on the viscosities and structural characteristics of sodium CMC and other disperse systems have been discussed at length by Hermans (17). Ott and Elliot (18) believe that thixotropy in sodium CMC solutions arises when chains of the CMC are bound together or cross-linked, giving regions of borderline solubility. This is further confirmed by the effects on sodium CMC solutions of polyvalent cations, particularly those having a high coordination number.

Timell (19) extracted a series of relatively low-D.S. samples rang-

ing from D.S. 0.075 to 0.36 with water. He found that for each sample the soluble portion had an appreciably higher D.S. and lower intrinsic viscosity than the original sample or the insoluble portion. He also found that the water-soluble, higher D.S. fractions had the same ratio (unity) of substituted primary hydroxyls to substituted secondary hydroxyls as did the original samples.

Daul, Reinhardt, and Reid (6, 20, 22) partially carboxymethylated cotton to obtain swellable fibers, and in a series of studies produced fibrous CMC with degrees of substitution ranging from 0.015 to 1.8. They found that carboxymethylation by their procedure had left the primary walls of the fibers intact to enable the observed ballooning of the sodium salt form in water. Increased tensile strength, swelling, water absorption, and changed dyeing characteristics were observed for cotton threads and yarns which had been partially carboxymethylated. The free acid form and most heavy metal salts of the CMC were found to be insoluble in water (6). Some of the metal salts were found to impart considerable resistance to microbiological attack on cloths made from low-D.S. CMC fibers.

Walecka (5) carboxymethylated rag pulp in alcoholic media to obtain low-D.S. CMC pulp fibers suitable for papermaking, varying in D.S. from 0.006 to 0.06. The low-D.S. CMC pulps showed higher handsheet strength properties than the untreated rag pulps, and the strength increase was obtained with less beating. This phenomenon was most pronounced for pulps in the sodium salt form; pulps which had been acidified with dilute acetic acid

(erroneously called the "free acid form" since CMC is a stronger acid than acetic acid) showed lower strength properties than the sodium salt form. An optimum in handsheet properties was found to exist at a D.S. of about 0.030. His observations on the low-D.S. CMC pulp and handsheet properties may be summarized as follows:

1. The pulps were not mercerized by the carboxymethylation.

2. Cupriethylenediamine viscosities showed that the rag pulp was degraded from a D.P. of about 2,000 to a D.P. in the range 900 to 1,300 during the carboxymethylation reaction. The degradation appeared to be independent of the D.S. obtained since the treated control (rag pulp treated similarly to CMC preparation but without any chloroacetic acid) was also degraded to the same extent.

3. There was a slight loss in the carboxymethyl content of the CMC fibers during beating and handsheet formation.

4. The beating time required to obtain a pulp of a given freeness decreased as the D.S. of the pulp was increased.

5. The bursting strength, tensile strength, and folding endurance of handsheets were increased with increasing D.S.

6. The tearing strength of handsheets varied only slightly with D.S.

7. The zero-span tensile strengths of handsheets and the initial increase in zero-span tensile strength with beating, both increased as the D.S. of the pulp was increased.

8. The porosity and opacity of the handsheets were decreased as the D. S. was increased.

9. The equilibrium moisture content of handsheets (73°F. and 50% R.H.) increased with increasing D.S. of the pulps.

10. Photomicrographs showed that the beaten CMC fibers retained more of their initial length and were broader, straighter, and more transparent than the fibers of the untreated pulps beaten to the same freeness. Also the fibrils formed from the CMC pulps were longer and more transparent than those in untreated pulps.

In addition to the above, Walecka found that the strength properties of the CMC pulps were quite different in the sodium salt and the "free acid" forms. The sodium salt forms of CMC pulp were stronger. No explanation of this difference in properties of the two forms was attempted.

ANALYSIS OF STRENGTH INCREASE

Besides its many other industrial usages, sodium-CMC at relatively high degrees of substitution is used as a beater adhesive in the paper industry. Addition of the CMC gum prior to sheet formation results in increased deflocculation of the pulp fibers and contributes to enhanced strength properties of the sheet obtained. A number of gums and mucilages find application as wet-end adhesives, in general contributing to better formation and increased sheet strength. A good review on the subject was made by Swanson (23), who discusses also the use of beater adhesives in terms of some of the pertinent concepts of fiber-to-fiber bonding.

Leech (24) in investigating the reasons for sheet strength increase

when locust bean gum is used as a beater adhesive, suggests four fundamental factors which may contribute to strength increase in a sheet of paper. These are:

1. The strength of fibers,
2. The strength of bonds,
3. The number of bonds,
4. The distribution of bonds (formation).

According to Leech, an increase in one or more of these factors should result in increased sheet strength. By utilizing tests designed to measure quantities related to the above, and by analyzing other sheet strength properties, he concluded that addition of locust bean bum contributes to better formation, a greater number of bonds, and a greater strength of bonds in a sheet of paper. These factors in turn influence sheet strength.

Low-D.S. pulps, as shown by Walecka, give increased sheet strength properties over the untreated fibers. If his data are examined in terms of the factors above, two pertinent facts emerge:

1. The zero-span tensile strength of the CMC pulp handsheets was increased with increasing D.S.

2. The tearing strength appeared to be affected little if any, by the substitution.

The zero-span tensile strength test (25) is supposedly a measure of the strength of the fibers. Leech (24) used it as such. This might indicate

that an increased strength of fibers could be involved in the low-D.S. carboxymethylation.

The absence of any change in tearing strength with substitution is more difficult to interpret. Since a decreased tearing strength is generally correlated with increased bonding in beaten pulps, it might appear that little, if any, change in the number of bonds may be involved in the strength increase of low-D.S. CMC pulps. However, both of the apparent suggestions above need closer examination before any conclusions may be drawn. The present work includes such an examination.

It is generally believed that hydrogen bonds are mainly responsible for the strength of a sheet of paper. Hydrogen bonding occurs when a hydrogen atom is shared by two strongly electronegative atoms such as oxygen, nitrogen, and even the halogens or sulfur. Such bonding can occur either intermolecularly or intramolecularly. In cellulose, which contains a number of hydroxyl groups in close proximity, such bond formation is very likely. Introduction of carboxyl or carboxymethyl groups in cellulose should not in any way hinder hydrogen bond formation.

On the contrary, substantial evidence is present in the literature to indicate that hydrogen bond formation is easier with carboxyl groups, and the bonds formed are appreciably stronger (27). Infrared absorption data for low molecular weight compounds give evidence of a definitely increased energy of the bonds for increasingly acidic hydroxyl groups (28).

Some of the more interesting literature on the subject is reviewed in Appendix I.

Carboxyl groups in pulp have often been considered to promote easier beating and earlier strength development (29). The suitability of CMC as an adhesive is ascribed to the presence of carboxyl groups in the polymer. In the case of synthetic polymer networks such as rubber, it has been experimentally shown that introduction of small amounts of carboxyl groups renders the polymer markedly susceptible to cross-linkage, resulting in very much increased strength and swelling properties (30). Thus, it is possible that stronger hydrogen bonds may be involved in the sheet strength increase of low-D.S. CMC pulps.

PRESENTATION OF PROBLEM

Low-D.S. CMC pulps have been prepared by Walecka (5). The reported method effects a substitution of rag pulp without noticeably changing the fibrous structure. It was found that low-D.S. carboxymethylation produced pulps which have higher sheet strength properties than the untreated rag pulp, and that the increase in strength is achieved with appreciably less beating. An increase in the hydrophilic nature of the CMC pulps is probably responsible. It is postulated that the carboxymethyl groups increase the degree of swelling of the fibers, permitting easier beating and the formation of stronger paper through the formation of larger bonded areas both within and between the fibers. The action has been likened to that of hemicelluloses in wood pulps. Moreover, the fibers themselves are considered to be stronger.

During the course of his study, Walecka observed that the sheet strength properties of CMC pulps in the "free acid" form were somewhat lower than those in the sodium salt form. The "free acid" form of the CMC was obtained by acidification with dilute acetic acid. No explanation of this phenomenon was attempted. It was felt that an investigation of low-D.S. CMC pulps in different "forms" would explain the changes in properties of the CMC pulps. Moreover, a thorough study of the changes should provide a mechanism for the primary phenomena noted above. The work reported herein covers such a study.

RAW MATERIALS

Walecka (5) carboxymethylated rag pulp. This material was chosen because of its high D.P. and its low content of noncellulosic material. The material was similar to that used by Bletzinger (1) and Aiken (2) in their studies on the acetylation of cellulose. The pulp prepared by Walecka was used throughout this study to enable comparison with his results. His procedure for the treatment of the rag stock is essentially outlined below.

A local rag paper mill supplied 50 pounds of their No. 1 hard rag stock prepared from unbleached, muslin-grade rags. The pulp had been prepared in a special laboratory-scale run, but the lime cook and hypochlorite bleach which the pulp received were equivalent to a mill-scale run. The pulp was obtained in the wet condition containing about 75-80% water, and was stored in pliofilm bags for a maximum of one week before being treated as described below.

Bletzinger (1) and Aiken (2) had found that the fibers of the original rag stock were too long to be handled satisfactorily in laboratory beating and sheetmaking equipment. They found that this difficulty could be overcome by cutting the rag stock in a laboratory beater at a very low consistency and for a short time. Walecka used a preparation similar to that of Bletzinger and Aiken. To provide a supply of raw material for the investigation, 28 pounds of the rag stock were cut at

0.3% consistency for 2 minutes in the 5-pound capacity Noble and Wood beater with 200 pounds on the bedplate. Periodic tests showed that the Schopper-Riegler freeness of the pulp batches varied from 720 to 740 cc. The cut pulp was partly dewatered by draining on a cloth-covered washbox and was then transferred to an experimental blow tank, where it was mixed for three hours with a 1 H.P. Unipower agitator and for an additional three hours with both the Unipower agitator and a 1/4 H.P. Lightnin' mixer. The pulp was allowed to drain overnight, dewatered on a desk-top Buchner, shredded and spread to air dry. When the pulp was dry, it was placed in Pliofilm bags for storage. This pulp was referred to by Walecka as "standard rag pulp". In the present thesis, this stored pulp (left over from Walecka's study and stored about 6 months) was used throughout. Other raw materials and chemicals, used for the CMC preparation and testing, have all been listed by Walecka (5).

DEGREE OF SUBSTITUTION DETERMINATION

Throughout this investigation, degree of substitution (D.S.) was determined by forming the silver salt of the carboxymethylcellulose with silver ortho-nitrophenolate. Sookne and Harris (31) used the reagent to estimate the base-combining capacity of cotton, and Elizer (32) utilized it to determine the carboxyl content of oxidized starches. Walecka (5) outlines the procedure as used for determining the degree of substitution of low-D.S. CMC pulps. The same method was used in this investigation and is briefly described below.

A 2-liter flask containing 15 grams of ortho-nitrophenol and 15 grams of silver oxide was warmed on the steam bath until the phenol melted. The mixture was stirred periodically and cooled to allow formation of a cake at the bottom of the flask. The reagent solution was prepared by simply adding distilled water and heating the mixture at about 60°C. for thirty minutes. After thorough shaking, the mixture was allowed to stand in order to obtain a saturated solution of the silver ortho-nitrophenolate as the supernatant layer. A hard core of excess reagent remained at the bottom of the flask, and could be used again for further dilution. The other reagents required were:

Standardized potassium thiocyanate, (0.02M).
Saturated ferric alum solution.
Boiled dilute nitric acid, (approximately 6N).

About 2 grams of the pulp were allowed to soak in dilute hydrochloric acid for 30 minutes in order to obtain the CMC in the free acid form. The acidified pulp was washed free of excess acid, then washed three times with absolute methanol, and allowed to dry overnight at 50°C. The methanol-dried fibers were next ground in a small Wiley mill, using a 20-mesh screen. The ground sample was allowed to dry again at 50°C. for over an hour. Moisture determinations of such samples were made by Walecka, who found the moisture contents too small to influence D.S. appreciably. Hence moisture determinations were not made in this investigation.

Duplicate or triplicate samples of the dry ground pulp were weighed (0.5 grams) and transferred to 125-ml. stoppered flasks. Fifty cc. of

the silver ortho-nitrophenolate solution were pipetted into each flask, and the flasks were stoppered, swirled, and set aside overnight.

The next morning, 25 cc. of the clear supernatant layer from each of the flasks were pipetted into 125-ml. Erlenmeyer flasks, and 5 ml. dilute nitric acid, 3 ml. ferric alum indicator solution, and 3 ml. nitrobenzene were added. The solution was then titrated to a reddish tinge with standardized potassium thiocyanate solution. The blanks were handled in a similar manner. The D.S. was calculated as done by Walecka.

PREPARATION OF LOW-D.S. CARBOXYMETHYLCELLULOSE PULPS

The procedure developed by Walecka (5) was used for preparing low-D.S. CMC pulps. In essence, the procedure consisted of methanol-benzene pretreatment of the rag pulp, and then a 30-minute soak in an appropriate solution of chloroacetic acid in isopropanol. The substitution was then accomplished by reacting the acid-soaked fibers with a boiling solution of 0.3% sodium hydroxide in 12.5% methanol-87.5% isopropanol for one hour. The mixture was stirred throughout the reaction period.

The substituted pulp was then thoroughly washed with deionized water and allowed to soak in a saturated sodium bicarbonate solution overnight, to obtain the sodium salt of the CMC. The detailed procedure has already been described by Walecka (5), who made a study of the different variables involved in the preparation.

Additional variables studied by Walecka included:

1. Pretreatment of rag pulp for increased accessibility.
2. Chloroacetic acid treatment (time and concentration).
3. Sodium hydroxide concentration, and time of reaction.
4. Washing variables.

The last variable, washing conditions, was further investigated in this study.

WASHING OF THE CARBOXYMETHYLCELLULOSE PULP PREPARATION

The washing procedure utilized by Walecka was as follows:

The acetic acid-neutralized pulp from the reaction vessel was washed four to six times, at one-hour intervals, with deionized water. After the final wash, an adequate sample of pulp was taken for D.S. and viscosity determinations. The bulk of the pulp was placed overnight in 20 liters of solution containing excess sodium bicarbonate in order to form the sodium salt of the carboxymethyl groups. The following day the pulp was washed eight to ten times, at one-hour intervals, with deionized water. The deionized water was found to be alkaline enough to maintain the sodium salt form of the CMC. The washed and dewatered pulp was stored in polyethylene bags in the cold room (40°F.) until used. It was noted that the higher D.S. pulps filtered much slower than did the low-D.S. or the control pulps. The pulps in the sodium salt form also filtered slower than did the same pulps in the "acid" form (5).

In the present study some of the washing variables were further investigated. The CMC pulp preparation was dispersed in deionized water, stirred thoroughly and allowed to stand for one hour. It was then filtered under suction using a Cenco qualitative filter paper, and the maximum possible water removal was effected by using a dental dam on the funnel in the final stages. The pulp was redispersed in deionized water and the process was repeated for each wash.

After the removal of excess methanol-isopropanol from the preparation, the first two washes were made with a dilute solution of acetic acid. The excess alkali in the mixture was thereby neutralized and removed to some extent in the subsequent filtrations. The filtration in this instance was accomplished with relative ease. The deionized-water washes which followed took much longer for each successive filtration. For a relatively high-D.S. pulp, for example, the filtration time for the wash with deionized water exceeded four hours, compared to about 5-10 minutes for filtration after the acetic acid wash. Similar phenomena were observed for lower D.S. pulps; the differences in the time involved were, however, less pronounced with decreasing D.S. The untreated[1] or the treated[2] control pulps, as would be expected, do not exhibit any noticeable difference in the time of the filtration even after many washes. The observations above are of necessity qualitative, but it is apparent that at any particular degree of substitution, the CMC pulps become harder to filter as they are washed free of the electrolytes present.

[1], [2], Footnotes are the same as at end of Table II p. 29.

Some mention should also be made of the change in appearance of the pulps during the washing steps. The rag pulp, originally white, was straw-colored as it came out of the reaction vessel. On neutralization with acetic acid, the white color was restored. Further washings did not affect the color.

The CMC pulps were flocculated and easy to filter at the acetic acid neutralization step. Even at high degrees of substitution the pulp was coarse and "dry" to the touch, not unlike the untreated material. At that stage, in fact, the untreated rag pulp, the treated control, and CMC pulps could not be distinguished from each other in physical appearance, dispersion characteristics, or the "feel" of the fibers. The differences began to appear after the first deionized-water wash and became more pronounced as the pulps were further washed. The pulps with relatively high degrees of substitution deflocculated considerably after washing, the supernatant became "milky", and the pulps felt "slimy". The control pulps remained unchanged through the washes.

THE SUPERNATANT LIQUID IN CARBOXYMETHYLCELLULOSE PULP SUSPENSIONS

A sodium salt form CMC pulp (D.S. 0.055), dispersed in distilled water, was found to have a very milky supernatant, and the fibers settled slowly. On centrifuging the pulp slurry (1600 rpm., 15 minutes) the supernatant liquid was freed of almost all of the fibers. The few fibers which persisted were removed by filtration through a fine fritted-glass filter funnel. The milky colloidal dispersion (pH approximately 8.0) was then collected in a flask, and various aliquots showed the following characteristics:

1. Further centrifuging, and even standing for fifteen days produced no visible separation of any solid material.

2. Under acidic conditions, using dilute hydrochloric acid, the colloidal dispersion was precipitated immediately and completely. The white precipitate settled leaving a clear supernatant liquid. The precipitation appeared to begin at a pH around 6.0 and was essentially complete at pH 2.0. On the alkaline side however, addition of sodium hydroxide produced no immediate precipitation. Above pH 10.0 appreciable settling took place if the solution was allowed to stand for 24 hours.

3. Addition of sodium chloride or potassium chloride had little effect on the colloidal dispersion. Addition of aluminum sulfate, barium chloride, zinc chloride, or copper sulfate resulted in precipitation.

4. The acid-precipitated material could be redispersed if the liquid was again made alkaline. The redispersion became difficult if the preci-

pitate was allowed to settle for any length of time.

5. The alkaline colloidal dispersion could also be precipitated by the addition of excess alcohol (ethanol or methanol). The filtrate after acid, or alcohol precipitation, did not give any further turbidity with alcohol or acid respectively, indicating that complete precipitation was effected by either reagent. Evaporation of the filtrate at reduced pressure showed an almost negligible solids content in the filtrate.

6. The white precipitate was flocculent and not fibrous in appearance. Under the microscope the precipitate resembled aggregated starch granules, rather than a fibrous residue. The material had a great tendency to dry out in lumps, and if extra drying precautions were not taken the material hornified into a solid mass. Such behavior, incidentally, has been found to be characteristic of isolated hemicelluloses from wood pulp.

SOME VARIABLES AFFECTING SEPERATION OF MATERIALS

To separate the fibers from the dispersed material, the CMC pulp suspended in water (pH 8.0), was dispersed in a British disintegrator. Filtration of the pulp slurry through a filter paper gave a relatively clear filtrate. On the other hand, if the slurry was filtered through a fritted glass filter funnel, the initially milky filtrate became clearer after a pad was formed. Besides, the filtration was slower after formation of the pad.

If the dispersed pulp slurry was centrifuged the supernatant liquid

could be decanted off. To separate some "floating" fibers, the colloidal dispersion could be filtered through a fritted glass filter. The remaining pulp was washed again a few times in order to obtain the maximum possible extraction of material under these conditions (pH 7.0 - 9.0). It was found early in the work that the original state of the fibrous preparation before extraction was quite important. Table I shows a qualitative comparative study with a CMC pulp (D.S. 0.035). The pulp, suspended in distilled water, was stirred vigorously and then treated as above.

TABLE I

EFFECT OF DRYING OF CMC PULPS ON SUBSEQUENT EXTRACTION WITH MILD ALKALI (pH 8.0)

State of Pulp, D.S. 0.035	Degree of Fiber Dispersion	Clarity of Supernatant Liquid
Water washed, undried	good	milky
Water washed, air dried	fair	clear
Water washed, O.D. (105°C.)	poor	clear
Water washed, methanol-benzene displaced	good	milky

The undried CMC pulp and the solvent-exchanged preparation exhibited similar behavior. No dispersion of any colloidal material occurred after air drying the preparation and allowing it to disperse in water even for extended periods of time (5 days) under continuous agitation. The oven-dried preparation could not even be dispersed again.

To obtain relatively quantitative and reproducible results the following procedure was adopted for all subsequent extractions:

The CMC preparation, washed thoroughly with water, was dried by solvent exchange with methanol and benzene successively. A weighed amount of the pulp (2.0) grams was suspended in distilled water (200 ml.) in a 250-ml. centrifuge bottle and the slurry was adjusted to pH 8.0 approximately (the phenolpthalein end point appeared to be quite suitable). The centrifuge bottle was stoppered and put on the shaker for one hour to disperse the pulp thoroughly.

The dispersed pulp was then centrifuged (1600 rpm., 10 minutes) and the supernatant liquid was decanted off through a weighed fritted-glass filter crucible. The remaining pulp was washed once with distilled water, the washings being collected with the main filtrate. The extracted pulp was then dried by solvent exchange with methanol and benzene successively, and weighed to determine the loss in weight.

TREATMENT OF THE EXTRACTED MATERIAL

It has already been indicated that the colloidal solution obtained above could be precipitated by acidification. A fairly reproducible method for collecting the precipitate, determining the weight and the degree of substitution was developed and is outlined below:

The slightly alkaline colloidal dispersion (the filtrate as obtained in the previous section) was acidified with dilute hydrochloric acid. The flocculent precipitate formed was allowed to settle for one hour. The

clear supernatant liquid was decanted off and filterd through a weighed fritted-glass crucible (medium). The precipitate was then quantitatively transferred to the filter crucible, filtered under suction, and washed free of excess acid with 50% methanol. (It was found that the precipitate was easily peptized with distilled water, and if washed with it, plugged the filter very easily extending the filtration for days). The collected precipitate was washed twice with absolute methanol, followed by two washings with hot absolute ethanol. The ethanol was finally displaced by a number of ethyl ether washes and the precipitate allowed to air dry. The crucible was then weighed again in order to obtain the weight of the collected material.

In order to obtain the material in a friable powder form, the following precautions had to be observed:

1. During all the filtrations and washing steps, the precipitate was never allowed to suck dry; a thin layer of liquid was was always retained on top.
2. In the final wash with ether, and the subsequent slow drying, the precipitate was ground continuously with a glass rod.

Without these precautions a hard granular material was obtained, or worse, under humid conditions, a tough dark "hornified" mass was formed.

DEGREE OF SUBSTITUTION DETERMINATION FOR THE EXTRACTED MATERIAL

The procedure using the silver ortho-nitrophenolate reagent had to be somewhat modified in order to determine the degree of substitution of

the extracted material. The modifications were necessary because of the friable powder form of the material and the rather small quantities used for the test.

The weighed filter crucible, containing a known amount of the extracted material, was placed in a 100-ml. beaker and 50 ml. of the reagent were pipetted through the crucible. The beaker was then covered with a piece of dental dam and a rubber band, and left standing overnight to attain equilibrium. After 24 hours, an appropriate amount of the reagent was drawn from the beaker and titrated with standard potassium thiocyanate according to the procedure already described.

THE MATERIAL EXTRACTED AND THE CARBOXYMETHYLCELLULOSE PULP

The material extracted by the above procedure was a white friable powder, in appearance quite similar to purified hemicelluloses from wood pulps. If dried it became difficult to redisperse in water. In slightly alkaline solutions, however, an appreciable portion appeared to disperse colloidally on sufficient agitation. Improperly dried material could not even be dissolved in concentrated alkali.

The CMC pulp appeared almost unchanged in physical appearance after the extraction. When observed under a microscope, some of the "debris" around the fibers seemed to have been removed by the extraction. The change, however, was not very conspicuous. The extraction did not alter the dispersion characteristics of the CMC pulp noticeably.

Considerable difficulty was experienced in obtaining reproducible extraction results. The data in Table II, however, give approximate values of the amounts extracted and the D.S. distribution of the materials achieved.

TABLE II

MATERIAL EXTRACTED AND D.S. DISTRIBUTION ACHIEVED BY EXTRACTION OF LOW-D.S. CMC PULPS AT pH 8.5

Pulp	Material Extracted, Weight, % O.D. pulp	D.S.	Extracted Pulp Loss in weight, % O.D. pulp	D.S.
D.S. 0.004				
Untreated control[1]	--	--	negligible	--
Treated control[2]	--	--	--	0.005
D.S. 0.031				
One extraction	2.4	0.12	3.5	0.028
Two extractions	4.2	0.11	5.2	0.028
Six extractions	5.5	0.15	--	0.030
D.S. 0.055	4.0	0.16	5.0	0.041

[1] Rag pulp solvent-exchange dried by means of methanol and benzene

[2] Rag pulp solvent-exchange dried by means of methanol and benzene, and treated to all the steps of the carboxymethylation procedure (concentration of chloroacetic acid : 0.0%)

It is apparent that appreciable amounts of nonfibrous material, with D.S. four to five times that of the CMC pulp, could be removed from the sodium salt form pulp under practically neutral conditions. Shaking of the pulp during extraction was found to be most critical. Little separation occurred if the CMC pulps were just allowed to soak in water without stirring. It is felt that a standardized method of shaking the pulp during extraction is essential for obtaining reproducible results.

Table II also shows that the extraction removed a relatively small percentage of the total substitution from the CMC pulps. The material removed displayed a considerably higher D.S., but, in fact, the major portion of the substitution was still retained by the CMC fibers. Very little material could be removed after about six extractions unless the extracted pulp was beaten lightly. In trying to improve on the D.S. determinations of the extracted material and to give a more quantitative basis to the experiments above, other methods including direct and indirect acid-alkali titrations were tried (33). The results were, however, disappointing and further attempts were abandoned.

METHYLENE BLUE ABSORPTION

Methylene blue absorption has often been suggested as a quantitative determination for the carboxyl group content of cellulose. For starches and like materials, where the carboxyl groups are relatively "accessible", a reaction time of 10 minutes has been considered to be quite sufficient (34). For cellulosic fibers, however, the dye has to be kept in contact

with the fibers for at least 24 hours in order to obtain a quantitative evaluation of the carboxyl content. A study of the effect of time, on the other hand, reveals that a major percentage of the dye absorption takes place in the first 15 minutes of contact (35). It appears that the relatively "accessible" carboxyl groups take up the dye in a very short time. It is also very likely that the carboxyl groups on the surface of the fibers would be the most "accessible" to the dye. Carboxymethyl groups obviously should also be expected to display a similar behavior. The results of a qualitative experiment with methylene blue absorption on a CMC pulp (D.S. 0.031) may be depicted as follows:

A very dilute solution of methylene blue (approximately 0.02%) was left in contact with each of the following materials for 15 minutes and 24 hours, respectively:

(a) untreated cotton,
(b) CMC (D.S. 0.031),
(c) extracted CMC (b), six extractions,
(d) lightly beaten (5 minutes in Jokro mill) extracted CMC (c),
(e) extracted and acid-precipitated material from the CMC (b).

After the appropriate time intervals, the excess dye was decanted off, and the materials were washed thoroughly with distilled water until the wash solution was practically colorless. The colors of the materials after methylene blue absorption for different times are indicated in the flow sheet below.

(a) UNTREATED COTTON

after 15 minutes: practically no dye take up
after 24 hours: very light blue

(b) CMC

after 15 minutes: deep blue
after 24 hours: deep blue

(e) EXTRACTED AND ACID PRECIPITATED MATERIAL

after 15 minutes: deep blue
after 24 hours: deep blue

(c) EXTRACTED CMC

after 15 minutes: no dye takeup
after 24 hours: deep blue

(d) EXTRACTED CMC, BEATEN

after 15 minutes: deep blue
after 24 hours: deep blue

The extracted pulp, with only 15 minutes contact with the dye solution, had the same color as the fibers of the untreated cotton. The color, however, deepened to a deep blue after 24 hours. The CMC, the extracted material, and the lightly beaten extracted pulp on the other hand, were dyed deep blue even after 10 minutes contact with the dye solution, and any further change in color could not be differentiated visibly. Since the removal of the material was accomplished at practically neutral pH values and without any drastic mechanical action on the fibers, the above suggests that the material with relatively high D.S. was removed primarily from the surface of the CMC fibers. Moreover, the findings in Table II appear to be qualitatively confirmed.

BEHAVIOR WITH DILUTE ALKALI SOLUTIONS

The observations made in the preceding sections involved extraction of the low-D.S. sodium CMC pulps under very slightly alkaline or practically neutral conditions. It was considered of interest to determine the effect of dilute alkaline extraction on the CMC pulps.

EFFECT OF STRENGTH OF ALKALI

Twenty five grams of a low-D.S. (0.029) CMC pulp preparation was washed successively with methanol, dilute acetic acid, and finally with distilled water. The wet pulp was then divided into seven parts. Six of the samples were extracted with alkali of increasing strength, while one sample was treated for a regular D.S. determination. Each of the six samples was put in 250-ml. centrifuge bottles and 100 ml. of 1, 2, 3, 6, 9, and 15% sodium hydroxide solutions were added respectively. The centrifuge bottles were stoppered, put on the shaker for 15 minutes, and then left in the refrigerator overnight.

After 24 hours, the pulp samples were centrifuged and filtered through coarse fritted glass crucibles. The filtrates were found to be clear in each instance, and no turbidity was produced even on dilution. The pulps were then washed with water, dilute hydrochloric acid, and treated for D.S. determination of each sample. The results are shown in Table III.

TABLE III

EFFECT OF STRENGTH OF ALKALI ON D.S. OF EXTRACTED PULP

Strength of Alkali, %	D.S.
0	0.029
1	0.028
2	0.027
3	0.023
6	0.024
9	-- (could not be filtered)
15	0.021

No yield of the extracted CMC pulp was measured. The above was solely concerned with the decrease in D.S. produced by alkali extraction. A caustic strength of 3% was chosen for further investigating the alkaline extraction of low-D.S. CMC pulps.

EXTRACTIONS WITH 3% SODIUM HYDROXIDE

Table IV shows the effects of 3% sodium hydroxide extraction on CMC pulps of increasing the D.S. The pulps were prepared in batches of 25 grams each, and the concentration of chloroacetic acid used in each instance was so designed as to give steadily increasing degrees of substitution. It is apparent that such an objective was not attained. It is felt that irregular stirring during the course of preparation might be responsible for the erratic D. S. values obtained.

The CMC pulps were washed with methanol and then dried after two washes with benzene. The extractions were carried out in centrifuge bottles, using two-gram samples of pulp and 100 ml. sodium hydroxide in each instance. The procedure followed has already been indicated. In this instance, however, the filtrates were acidified and D. S. determinations were made on the precipitates which were formed. The weight of the precipitated material and loss in weight of extracted pulp were also determined in each instance.

The data in Table IV make it evident that the action of 3% sodium hydroxide on low-D.S. CMC pulps is quite different from the extractions at pH 8.5 (Table II). The treated- and untreated-control pulps differ markedly under the action of 3% sodium hydroxide. The loss in weight of the treated control, with no substitution, is approximately similar to the values obtained for the low-D.S. CMC pulps. Increased alkali solubility is generally considered to be good evidence for degradation in cellulose. These results confirm Walecka (5), who found appreciably decreased viscosities for the treated control and low-D.S. CMC pulps when compared to the untreated rag pulp. He also found that the viscosities of the low-D.S. pulps and the treated control pulp were essentially similar. The 3% sodium hydroxide solubility data above is thus seen to confirm Walecka's conclusion that the major portion, if not all, of the degradation observed in low-D.S. CMC pulps was due to the action of the alcoholic alkali. The mechanism of the accelerated action in the degradation with alkali at a relatively low concentration may be analogous to that

TABLE IV

EXTRACTION OF LOW-D.S. CMC PULPS WITH 3% SODIUM HYDROXIDE

	Preparation of CMC		3% NaOH-Extracted CMC		Acid-Precipitated Extract	
Pulp	Concentration of $ClCH_2COOH$, %	D.S.	Loss in Weight of CMC, % (O.D.)	D.S.	Weight Precipitate, % CMC (O.D.)	D.S.
I	untreated control	0.004	— (slight increase)	0.006	0.3	—
D	treated control	0.005	5.7	0.007	0.2	—
F	0.5	0.017	5.2	0.021	1.1	0.28
B	1.0	0.031	6.5	0.036	1.3	0.25
G	1.5	0.035	6.3	0.041	0.9	0.35
A	2.0	0.037	6.3	0.043	1.8	0.35
H	2.5	0.041	7.3	0.050	1.9	0.19
C	3.0	0.034	6.6	0.038	1.9	0.32
E	4.0	0.041	6.4	0.050	1.6	0.23

proposed by Valley (14) for accelerated acid hydrolysis of cellulose in alcoholic media, as has been discussed in the introduction.

DISCUSSION

Observations in the preceding sections show that by carboxymethylating cellulose in alcoholic media we have been able to get an appreciable penetration of the reaction in the fibrous structure, thus effecting substitution on the internal surface of the fibers. Exhaustive extractions of the low-D.S. sodium CMC fibers at pH 8.5 removed material which displayed a much higher D.S. A major portion of the substitution, however, was retained by the fibers and could not be removed even by cold dilute alkali extraction.

It is also apparent that the reaction was not uniform, since we could easily remove higher D.S. material from the fibers. In view of the experiments with methylene blue, extraction at pH 8.5 probably succeeded in removing material only from the external surface of the fibers. Since mechanical agitation was so very important in this extraction, and since a reasonable balance of materials and substitution could be obtained (Table II), it seems that higher substituted portions of the external surface of the fibers were "solubilized" in the sodium salt form. In opening up the fiber structure and exposing more of the internal surface, mechanical beating presumably brings more of these higher D.S. fiber segments to the surface.

As evidenced by the data in Table IV, the action of 3% alkali on low-D.S. CMC pulps appears to be markedly different from the "solubilizing" action of extraction at pH 8.5. The 3% sodium hydroxide dissolved an appreciable amount from the fibers, but acid precipitation of the solution yielded only a very small percentage of the material dissolved. The treated control and the untreated control pulps differed markedly in 3% alkali solubility; the loss in weight for the treated control (without any substitution) almost approached that of the low-D.S. CMC pulps. Extraction at pH 8.5, on the other hand, showed that while both the treated- and the untreated-control pulps did not show any loss in weight, increasing substitution appeared to "solubilize" more of the higher D.S. material from the CMC pulps. Inspection of data in Table IV shows that there was an increase in the carboxy content of the pulps after extraction with 3% alkali, indicating that alkaline oxidation must have taken place, resulting in the formation of new carboxyl groups. This was not found to be the case for extraction at pH 8.5 (Table II).

In explaining the different behavior of low-D.S. CMC pulps under alkaline and acidic conditions reference should be made to the works of Reid and Daul (6, 20, 22), who have described the properties, especially the solubility characteristics, of a number of salts of partially carboxymethylated cotton. Even relatively low molecular weight CMC is found to be insoluble in the free acid form. In low-D.S. CMC pulps, this may be reflected in the tendency of the pulps to flocculate under acidic conditions. The extracted nonfibrous material from the pulp was

also precipitated by acid. Acidification of the sodium CMC fibers may thus result in a precipitation of the colloidally dispersed ("active") hydrophilic substituted portions of the fibers, resulting in decreased surface area. Similar considerations should be applicable to the effects of other ions which give insoluble CMC salts.

CMC PULPS IN SUSPENSION

A number of preliminary observations revealed that CMC pulps in water suspension were extremely sensitive to the presence of various ions in solution. Addition of certain electrolytes resulted in immediate flocculation of the pulps. From qualitative experiments it appeared that action of cations was primarily responsible for the behavior. Hydrogen ions and polyvalent metal ions were most effective, while alkali metals and anions, in general, did not produce appreciable changes at least for the relatively low concentrations used.

It might be relevant to observe that cations, which are known to yield insoluble salts of relatively high D.S. carboxymethylcelluloses, flocculated the pulps quite readily. At lower concentrations of these cations, where the flocculation of the pulps was not very apparent, changes in a number of other pulp properties were found to occur. The S.-R. freeness and filtration resistance values, for instance, change markedly with electrolyte concentration.

Schopper-Riegler (S.-R.) freeness and filtration resistance are

measures of the rate of drainage of pulps. The freeness test, however, has been found to be influenced by a number of factors, including "wetness", fibrillation, length and stiffness of fibers, surface of fibers, and the formation of the fiber mat (36). It is, in general, not amenable to further analysis. Filtration resistance data on the other hand, can be analyzed into components of specific surface, effective specific volume, and compressibility, to yield fundamental information on changes in pulps (37).

SCHOPPER-RIEGLER (S.-R.) FREENESS STUDIES

A batch of rag pulp (700-grams) was carboxymethylated to a D.S. of 0.035. On completion of reaction, the pulp was washed with dilute acetic acid, excess acid being subsequently removed by a number of washes with distilled water. In order to obtain the sodium salt form of the CMC, the pulp was then soaked overnight in a solution of sodium bicarbonate. After washing thoroughly with distilled water, the pulp was divided into six equal portions and beaten in a Jokro mill for intervals of 0, 4, 8, 12, 18, and 24 minutes, respectively.

The S.-R. freeness determinations were made using Institute Method 414. Freeness changes were determined as a function of pH as well as alum concentration. All dilutions of the pulp slurry were made with distilled water. The freeness sample was diluted to just below one liter, the necessary amount of electrolyte was introduced, and the slurry brought up to the mark with water. The freeness was then determined after

a thorough mixing of the sample. The time interval between electrolyte addition and freeness determination was kept to a minimum in each instance. Adjustments of pH were made with dilute solutions of sulfuric acid or sodium hydroxide, while alum was pipetted as a dilute solution of $Al_2(SO_4)_3 \cdot 18H_2O$ of known strength. A pH meter with a glass electrode was used for pH measurements. Since no consequential differences were found when either the slurry or supernatant pH was measured, only pH values of the slurry are indicated in the following.

The Effect of pH

Figure 1 shows the very marked effect of pH on the S.-R. freeness of a low D.S. (0.035) CMC pulp at various degrees of beating. It is evident that while the freeness was almost unaffected in the alkaline range, increasing acidity produced sharp rises in the freeness values. The effect is found to be most prominent in the unbeaten pulp. The freeness of the unbeaten pulp appeared affected even at pH 6.5, while after beating for 24 minutes in a Jokro mill, the CMC pulp was almost unaffected at a pH as low as 4.0. The pH sensitivity of the low-D.S. CMC pulp, as reflected by the rise in freeness under acidic conditions, is thus seen to decrease with increased beating.

The low-D.S. CMC pulps flocculated appreciably at lower pH values. It was difficult to mark the exact pH at which the flocculation begins, but below about pH 4.5 the flocculation was quite distinct. The change

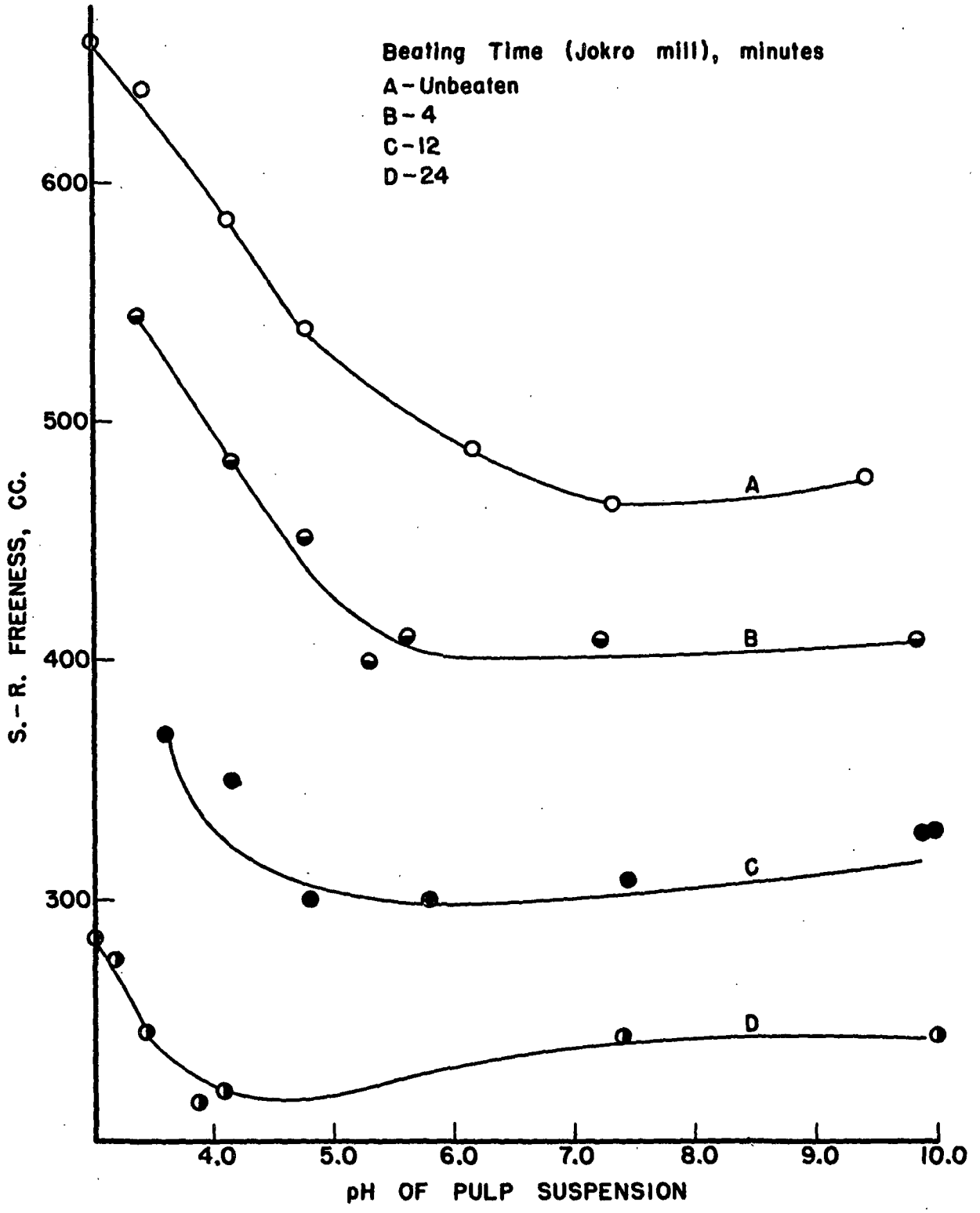

Figure 1. S.-R. Freeness Versus pH of CMC (D.S. 0.035) Pulp

in freeness, however, commenced at relatively higher pH values even at pH 6.5 for the unbeaten pulp, where little flocculation, if any, was perceptible. Further observations on the effect of pH may be summed up as follows:

1. The pH range investigated in all instances was restricted to 3.5 - 9.5 for fear that higher acidity or alkalinity might damage the freeness tester.

2. The treated and the untreated control pulps were not affected noticeably by pH, at least in the range investigated above.

3. When the pH was adjusted by means of sulfuric acid or sodium hydroxide, the effect on the pulp was quite reversible. Thus, the freeness of a low-D.S. CMC pulp at pH 7.0 could be reproduced, if the pH of the slurry was first reduced to 3.5 and then taken up to 7.0. Similarly, the freeness of two samples at pH 3.5 were not appreciably different, if one was initially made alkaline and then acidified to pH 3.5. Reversibility was impaired, however, if too much electrolyte concentration was allowed to build up.

4. The change in appearance of the CMC pulp slurry, as manifested by flocculation or dispersion, was almost instantaneous with adjustment of pH.

5. The measured effluent also changed in appearance with variations in pH. The colloidally dispersed "milky" material at higher pH values was flocculated under acidic conditions. As the pH was further lowered, the flocs were found to decrease in quantity probably because of a more

difficult passage through the pulp mat. The effluent thus becomes clearer with decreasing pH.

6. The exclusion of extraneous ions from the system was found to be essential. Presence of even relatively small amounts of polyvalent ions for instance, seriously affected the results and quite often obscured the whole phenomenon. The S.-R. freeness variations for CMC pulps in tap water were found to be rather high. Moreover, especially during the summer months, the low-D.S. CMC pulps were completely flocculated if suspended in tap water, even at alkaline pH values. Hence, distilled or carefully deionized water had to be used for all dilutions.

7. It was found that barium, aluminum, ferric, zinc, and cupric ions, cations which are known to yield insoluble salts of carboxymethylcelluloses, flocculated the low-D.S. CMC pulps. Furthermore, even beaten CMC pulps assumed the "feel" and appearance of unbeaten untreated fibers in the presence of these metal ions. In striking contrast, the alkali metals, known to yield soluble carboxymethylcelluloses, tended to disperse the CMC pulp slurry, and even unbeaten CMC fibers gave the feel and appearance of "hydrated" pulps.

The Effect of Alum on the Freeness of Low-D.S. Carboxymethylcellulose Pulps

Due to the widespread usage of alum in the paper industry, the trivalent aluminum ion was naturally selected to further investigate the effect of cations on the properties of low-D.S. CMC pulps. S.-R. freeness determinations were made with varying concentrations of aluminum

sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$) in the pulp suspensions. Appropriate amounts of a dilute solution of the alum were pipetted to the freeness sample, and the determinations were made immediately after thorough stirring of the pulp suspensions.

Figure 2 shows the almost remarkable effect of alum concentration on the S.-R. freeness of a low-D.S. (0.035) CMC pulp at various degrees of beating. The pulp was beaten to the appropriate time interval in a Jokro mill. It is apparent that the addition of alum changed the freeness of the pulp rather drastically. Attention may be drawn to the really low concentrations (of the order of 10^{-5} molar) of alum which were involved. At the concentrations of alum, the freeness of untreated rag pulp was unaffected, while the treated control appeared to show a relatively small rise in freeness.

It may be noticed in Figure 2 that the freeness is plotted against pH of the slurry achieved by the addition of alum. The approximate concentrations of alum used to attain the specific pH values are also indicated. Since the same batch of CMC pulp was used to collect data for Figures 1 and 2, respectively, the curves in the two can be compared. On comparison, it is immediately realized that the effect of alum is quite distinct from the effect of pH per se. It would appear that the concentration of aluminum sulfate is the primary and dominant variable. As seen in Figure 1, sulfuric acid exerts relatively little effect on the freeness of the CMC pulp in the pH range 8.0 to 5.0. In the same pH range, Figure 2 shows that alum produced rather marked changes in freeness. The differentiation between the effect of alum and pH is dealt with further on. It may be pointed out, however, that similar

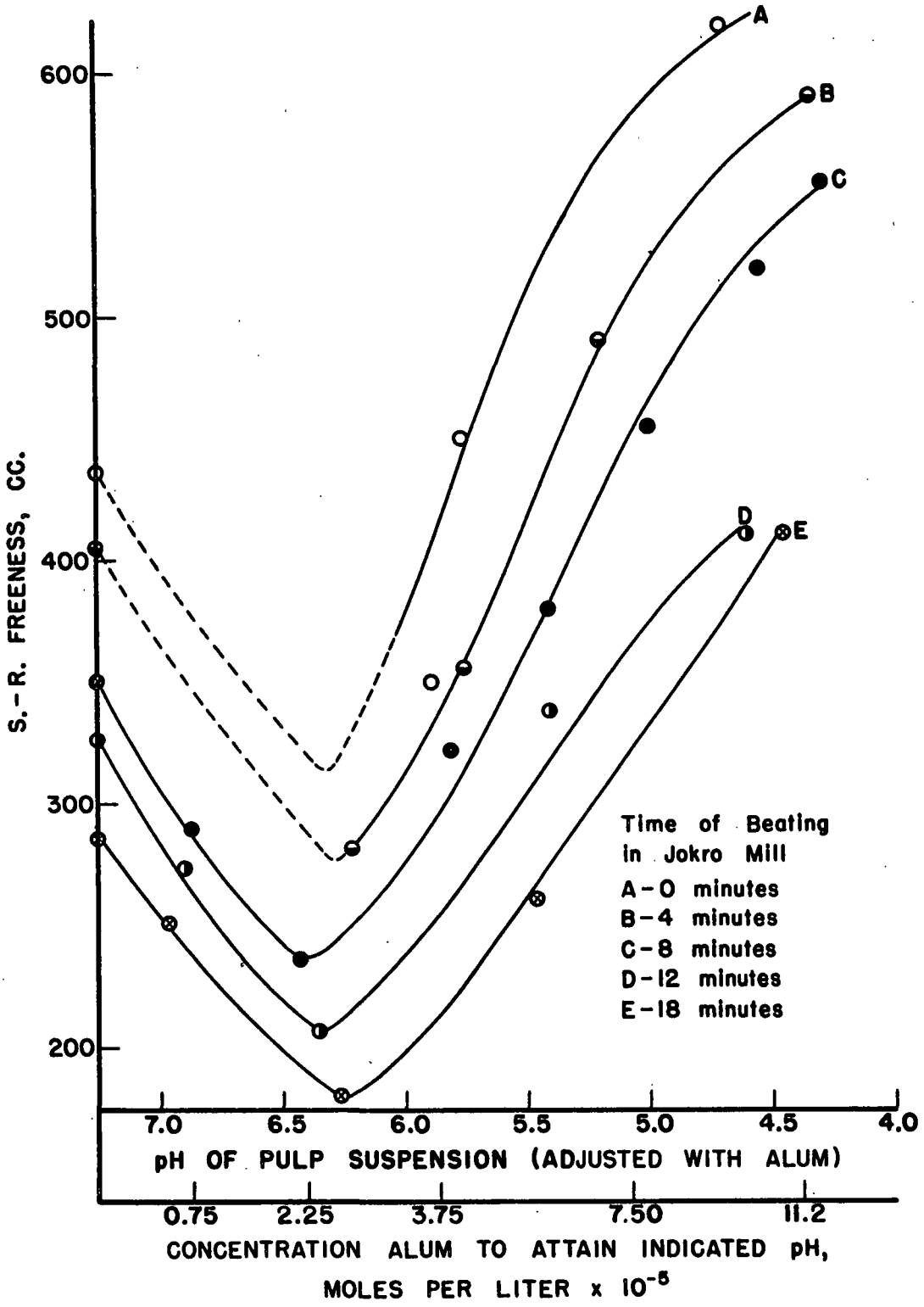

Figure 2. S.-R. Freeness Versus pH Adjusted by Alum for Beaten CMC Pulp (D.S. 0.035)

changes were produced by alum even if the pH of the pulp suspension was controlled at pH 7.0 by means of dilute sodium hydroxide. Some possible implications of the above are discussed in Appendix II.

It is also evident from Figure 2 that the beaten CMC pulp behaved similar to the unbeaten, as far as the effect of alum is concerned, except for a general lowering of the freeness curves with increased beating. It is surprising that the alum concentration required to arrive at the point of minimum freeness in each case is relatively independent of the degree of beating. This concentration of alum was found to be relatively constant for pulps of the same degree of substitution even from different batches of preparations. It may be mentioned, once again, that the concentration of alum required to produce the initial decrease in freeness, and better dispersion of CMC fibers, is rather low. It was almost missed entirely in the early stages of this study. Moreover, in the presence of other metal ions, which might be present in tap water, the effect was entirely obscured and only flocculation of the CMC was observed.

Figure 3 presents the effect of degree of substitution on the S.-R. freeness-alum concentration curves of CMC pulps. It is evident that the effect of alum was enhanced with increasing D. S. Alum caused an initial decrease and a subsequent increase of freeness, the effect being more pronounced with increasing degrees of substitution; the treated control showed only the increase of freeness. The untreated rag pulp showed no noticeable change in freeness in the range of alum concentration considered. With increasing D. S. the changes in freeness were found to become

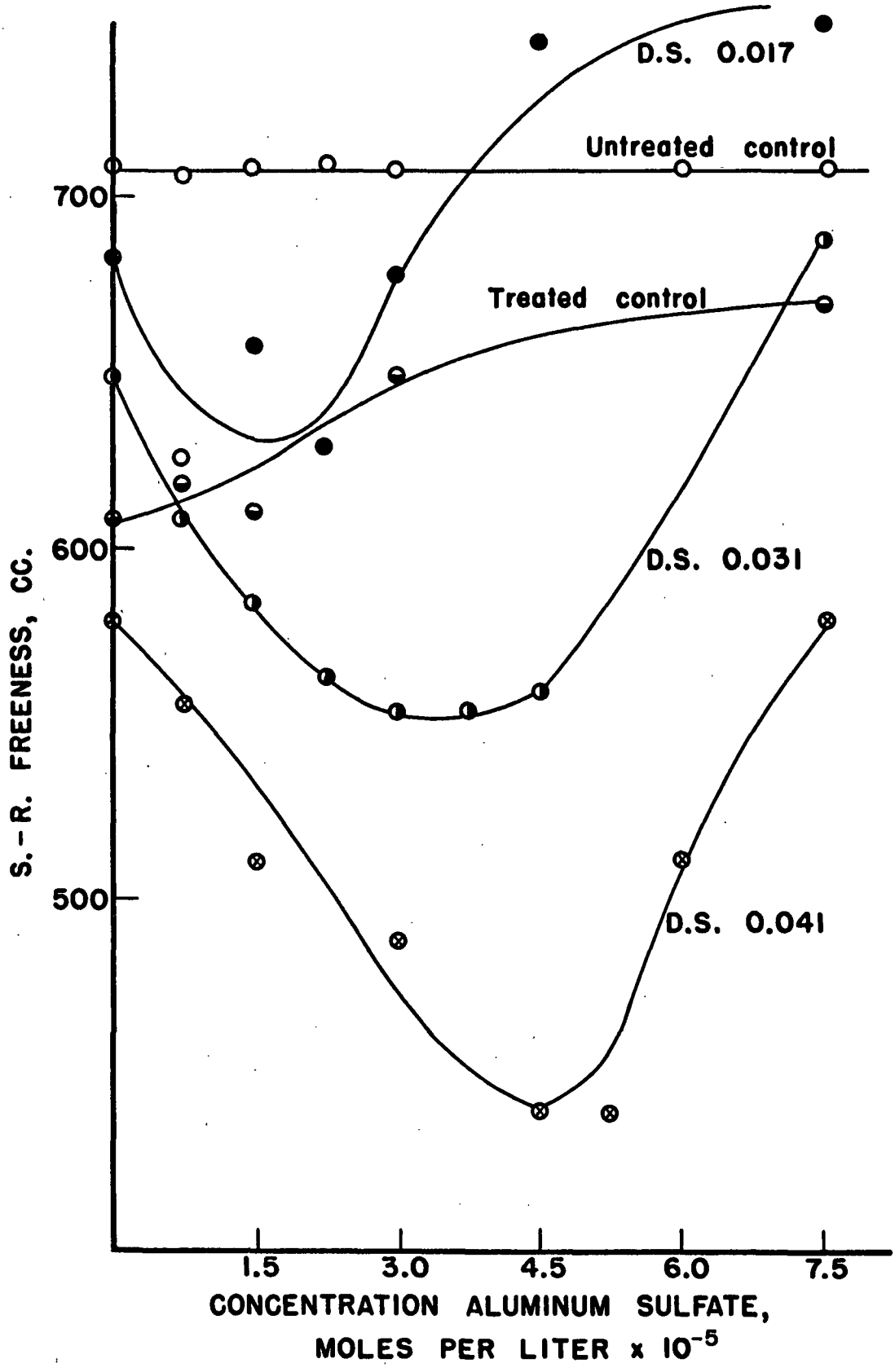

Figure 3. S.-R. Freeness Versus Alum Concentration for Unbeaten CMC Pulps

sharper and the minimum of the curves more defined. Furthermore, the minima of the curves tended to shift towards increasing alum concentration with increasing degrees of substitution.

FILTRATION RESISTANCE

The average specific filtration resistance has been proposed as an important property of papermaking fibers. The concept is evolved from the application of dynamic filtration principles to flow through compressible materials. Ingmanson (37) reveals that the Kozeny-Carman equation can be used to relate these principles to the important fiber properties of specific surface S, effective specific volume v, and compressibility c, which in turn form the basic components of the specific filtration resistance. Since they are amenable to further analysis, filtration resistance data, in contrast to S.-R. freeness data, can be expected to provide a more fundamental elaboration of the changes above.

The filtration resistance data presented below were collected by the Chemical Engineering Department at the Institute. The theory, technique and apparatus involved in constant-rate filtrations have already been described by Ingmanson (37, 38).

Figure 4 shows the filtration resistance curves (A, B, C, and D) obtained for CMC pulps with varying degrees of substitution. The pulps were in the sodium salt form and deionized water (pH approximately 8.5) was used for the filtrations. At any given pressure drop, the filtration

resistance is found to increase with an increasing degree of substitution. This is to be expected in view of the freeness data already presented.

Curve E in Figure 4 is of particular interest. Here tap water, with pH adjusted to 8.5, was used for the filtrations. The filtration resistance values for all of the pulps above fall approximately on this curve. The same curve was obtained when the filtration resistance was measured in the presence of sufficient alum in deionized water. The pulps displayed a tendency to flocculation in both instances, the tendency being most marked at higher degrees of substitution.

We thus see that low-D.S. CMC pulps in the sodium salt form give higher filtration resistance values at increased degrees of substitution, but only when the system is relatively free of extraneous ions. When sufficient amounts of other ions, probably polyvalent metal ions, are present in the water, the filtration resistance appears to be reduced to the same low level irrespective of the D.S.

Figure 5 shows the effect of increasing alum concentration on the filtration resistance of a CMC pulp. Curves A-E illustrate the very marked increase in filtration resistance at low concentrations of alum, and the equally steep decline when further alum is added. Examination of Figure 5 shows that, if the filtration resistance at a given pressure drop be plotted against alum concentration, a sharp maximum will be found, in approximately the range of alum concentration as the minimum in S.-R. freeness depicted in Figure 2, for the same D.S. pulp. Curve E apparently

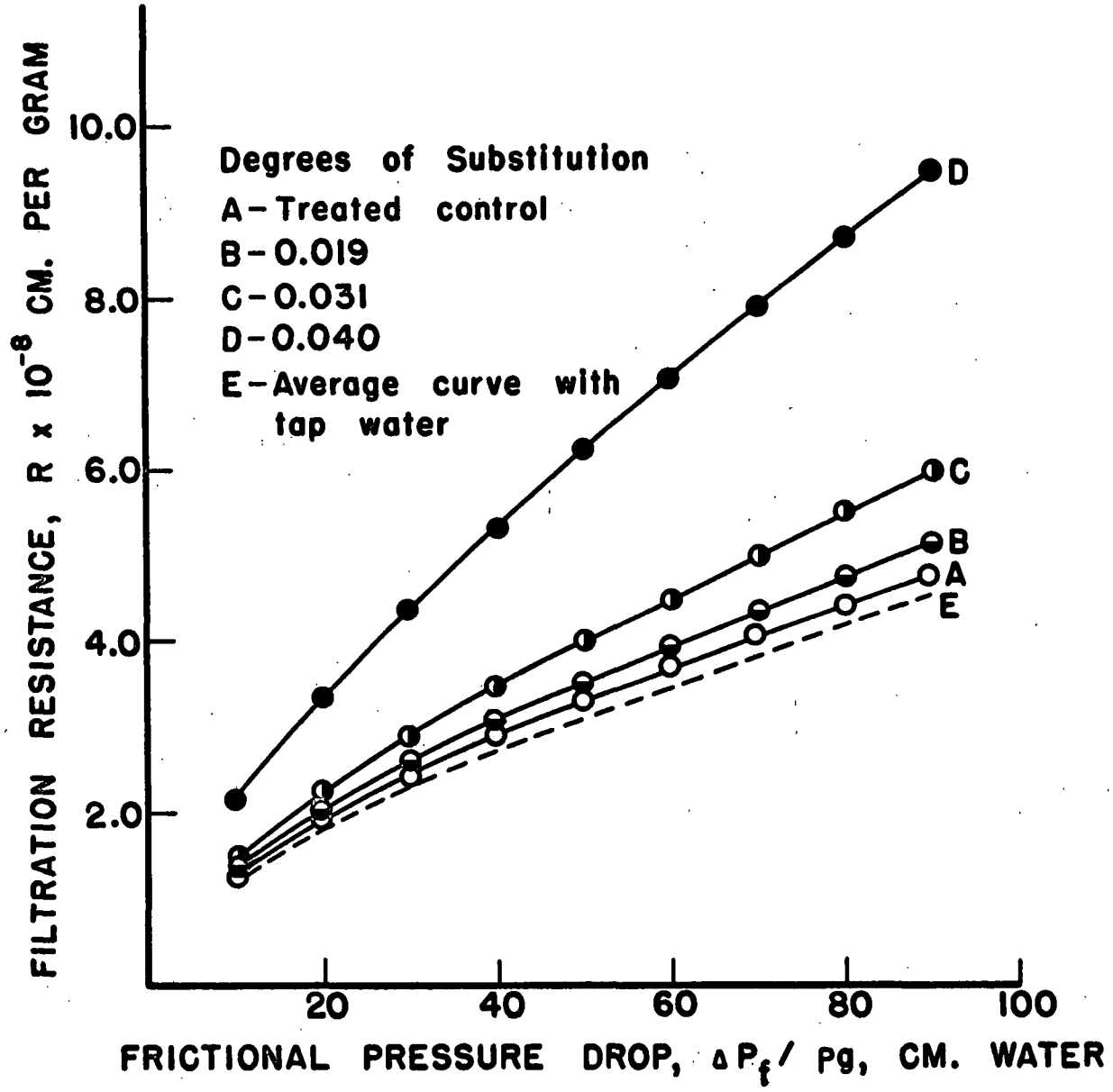

Figure 4. Filtration Resistance of Low-D.S. CMC Pulps

gives a limiting value, since no further change was found with additional alum.

Attempts were made to determine the effect of pH on the filtration resistance of low-D.S. CMC pulps. The copper mixing tank of the filtration apparatus, however, discolored the pulps and produced intense flocculation even under mildly acidic conditions. The attempts were therefore abandoned.

In general, the filtration data above clearly confirm the observations already made with S.-R. freeness. It would perhaps be logical to expect such a substantiation, except that general correlation between the two tests has been found to be rather poor (38). The freeness test is found to be quite insensitive in the high freeness range and relatively very sensitive in the medium freeness range, thereby becoming a rather rough and peculiar index of filtration resistance. The close confirmation between the two tests for unbeaten CMC pulps is therefore quite interesting. It points to the presence of (perhaps only a few) common factors powerful enough to override the differences inherent in the two tests.

Compressibility, Specific Surface, and Effective Specific Volume

Ingmanson's (38) equipment and procedure were used to measure compressibilities of the CMC pulps involved in curves A, B, and D of Figure 4. The results are plotted in Figure 6. Curve A (in Figure 6) was common to both the treated and untreated control pulps, indicating that no change

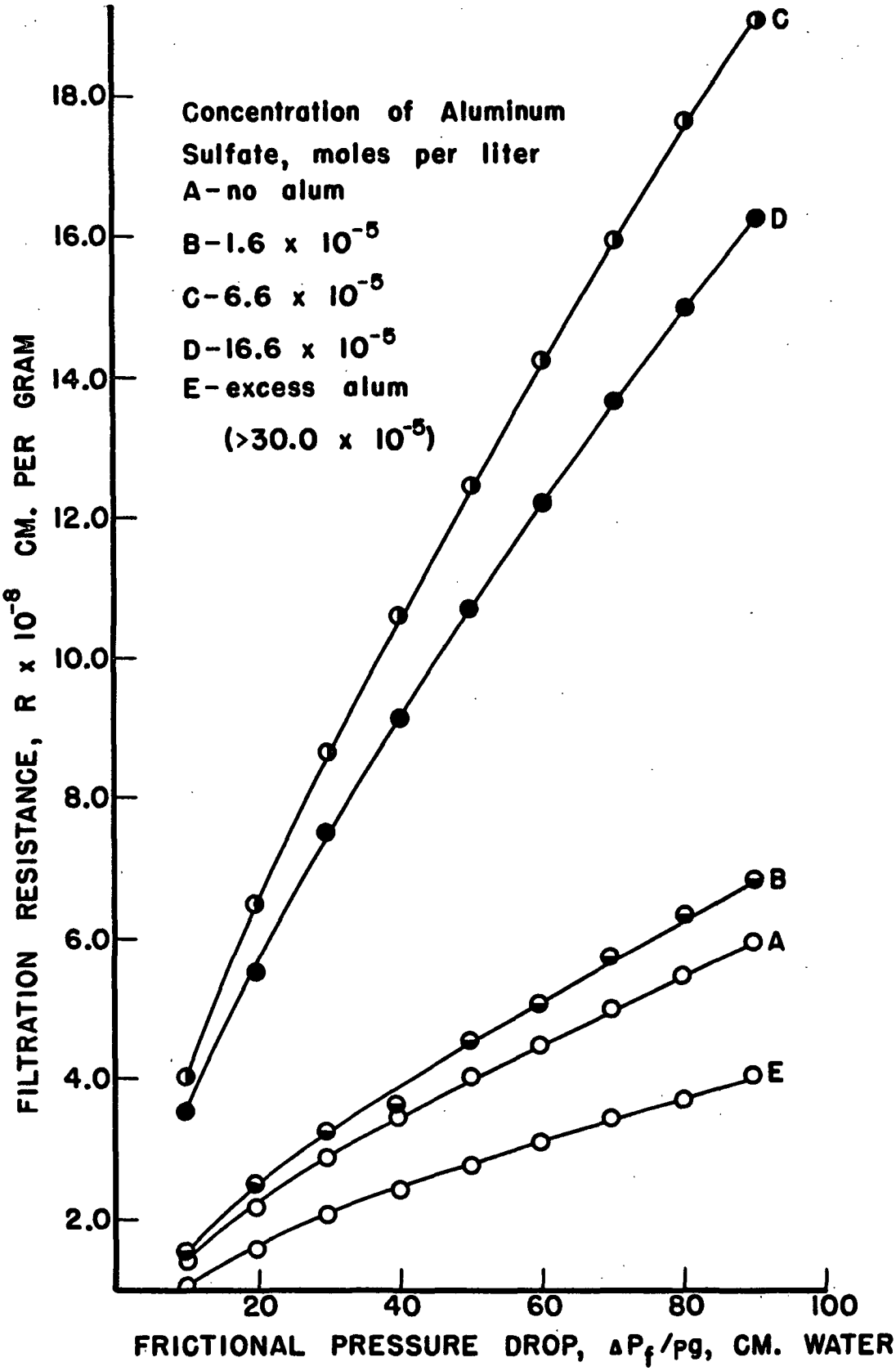

Figure 5. Effect of Alum on Filtration Resistance of Low-D.S. (0.031) CMC Pulp

in compressibility, per se, occurred due to the conditions of the carboxymethylation treatment. Curves B and C show the changes in compressibility with increasing degree of substitution for the sodium salt form of the CMC pulp.

These marked changes in compressibility are rather surprising. Ingmanson found that even considerable beating of pulps fails to change compressibility values. The compressibility as measured can almost be taken as a pulp characteristic which remains constant through the beating cycle. Constant compressibility provides a sensible basis for calculating increases in specific surface and effective specific volume due to beating for any given pulp.

The specific surface and effective specific volume values calculated from filtration resistance and compressibility data for a few pulps (unbeaten) are listed in Table V. (Curves A, B, and D in Figure 4 give the filtration resistances, while curves A, B, and C in Figure 6 give the compressibilities for the respective pulps involved.)

TABLE V

THE SPECIFIC SURFACES AND EFFECTIVE SPECIFIC VOLUMES OF LOW-D.S. SODIUM-CMC PULPS (UNBEATEN)

Pulp D.S.	Specific Surface, S, sq. cm./g.	Specific Volume, v, cc./g.
0.002 (treated control)	20,250	1.48
0.019	19,600	2.14
0.040	22,800	2.32

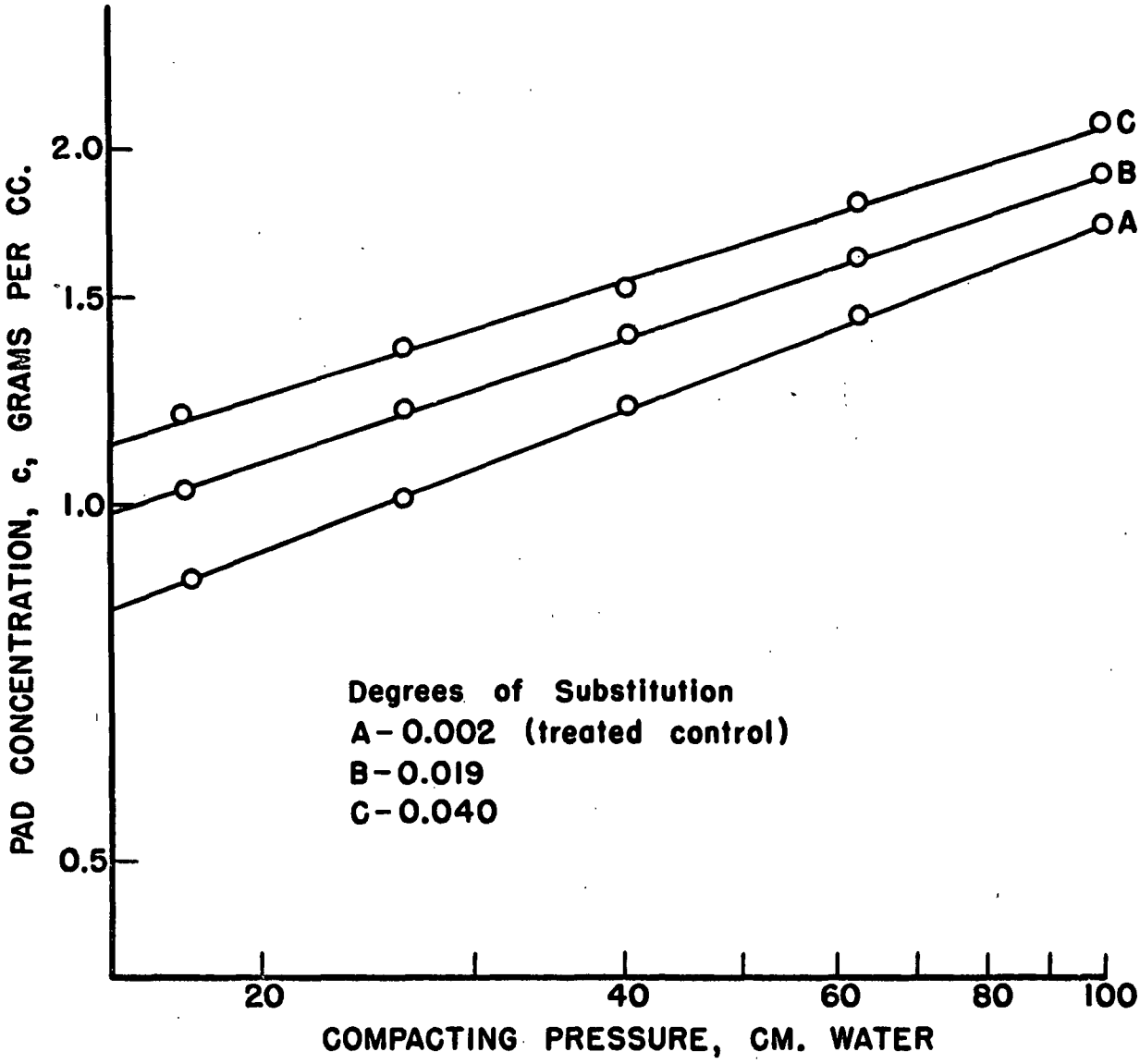

Figure 6. Compressibilities of Low-D.S. Sodium CMC Pulps (Unbeaten)

Table V shows that while the specific surface remains practically unchanged with increasing substitution, the specific volume is increased considerably. For the sake of comparison, it may be recollected that the change in the calculated specific volume of a pulp for a full beating cycle is of the order of 1.0 cc./g.

An analysis of the filtration resistance into its components thus reveals that the specific volume and compressibility of the rag pulp is increased by substitution of sodium-carboxymethyl groups. The calculated specific surface on the other hand, appears practically unaffected. In contrast, a similar increase in specific volume of pulps by mechanical beating would inevitably be accompanied by a manifold increase in specific surface, while the compressibility would hardly be affected. We thus find a fundamental difference between the action of mechanical beating and carboxymethylation of fibers being pointed out by filtration resistance analysis.

In view of the above, the evaluation of filtration resistance of CMC pulps in acid form, or in the presence of various metal ions, assumes high importance. Unfortunately, the intense flocculation of low-D.S. CMC pulps under such conditions makes the results quite erratic and unreliable. It has already been shown, however, that the presence of sufficient alum in the system reduces the filtration resistance of CMC pulps to values even somewhat less than those of the control samples. On the basis of the freeness experiments, it is rather safe to expect similar behavior in the

presence of acid. Slightly acidified CMC pulp slurries do, in fact, show decreased filtration resistance and compressibility.

We thus find that while CMC pulps in the sodium salt form show vastly increased effective specific volumes and compressibilities, the acid form would show no such changes over the control pulps. The calculated specific surface values do not appear to change in any one of the above operations. This behavior makes it worth while to look more closely at the basis of filtration theory as applied in the present instance and discussed below.

According to Ingmanson (38), mechanical beating of pulps results in increased average specific filtration resistance. When analyzed in terms of S, v, and c, the components of filtration resistance, marked increases are found in the specific surface and effective specific volume, while the compressibility remains practically unchanged. The absence of a change in compressibility, which may be considered as a measure of fiber flexibility, is found rather surprising. Ingmanson (39) tends to believe that the compressibility is probably altered, but that compensating factors, such as fines in beating, mask the change. He considers it more realistic to postulate an actual increase in compressibility in terms of the ratio of the specific volumes calculated from the filtration resistance. Such an argument seems reasonable enough, since fibrillation in beating would naturally be expected to produce more flexible fibers.

For unbeaten CMC pulps, however, the compressibility values are

found to vary appreciably even with pH. It is hard to believe that fiber flexibility could really be involved in this very reversible and instantaneous behavior. Besides, the specific volume values are changed, but the calculated specific surface remains essentially the same under these conditions. The specific volume change in this instance appears to be always accompanied by a corresponding compressibility change in the same direction. If we consider this change in compressibility value in the light of Ingmanson's argument above, the changes then assume a somewhat unreal character. Interpretation of the results is thus exceedingly difficult and risky, until more is known of the quantities S, v, and c, as derived from filtration experiments.

VARIABLES CONNECTED WITH THE EFFECT OF ALUM

The preceding pages show that addition of alum exerts a marked effect on the S.-R. freeness, filtration resistance, and dispersion characteristics of low-D.S. CMC pulps. The effect of alum can be divided into two rather distinct portions. At very low concentrations, and up to an optimum concentration, which appears to depend on the D.S., increasing the concentration of alum resulted in decreased freeness, higher filtration resistance, and improved dispersion of the CMC pulps in suspension. At concentrations higher than the optimum concentration, the action of alum was reversed, increasing concentration resulting in higher freeness, decreased filtration resistance, and a marked flocculation of the

pulps. This reversal appears to be peculiar to alum, since the addition of hydrogen ions, and the other metal ions (barium, ferric, zinc, and copper) produced only increased freeness and flocculation of fibers, in the low-D.S. CMC pulp suspensions. Thus, the effect of alum at relatively higher concentrations was similar to that of the other cations, which is as would be expected, but at lower concentrations it is reversed. The interests of this study are only concerned with the effect of alum in the relatively higher concentration range. Some of the variables which control the unique behavior of alum (in decreasing the freeness of CMC pulps) at very low concentrations, however, were studied for more information on the phenomenon.

The Effect of pH on the Addition of Alum

The effect of pH of the slurry on the action of alum is shown in Table VI. The data in section (a) determined the concentration of alum (1.5×10^{-5} moles per liter) required to obtain the minimum in S.-R. freeness and optimum dispersion of the low-D.S. (0.035) CMC pulp slurry at a constant pH. For the data in section (b), the above concentration of alum was used and the pH of the pulp slurry was varied by the addition of either sodium hydroxide or sulfuric acid. It was found that the reduction in freeness of the unbeaten pulp, due to the presence of alum at the concentration above, was maximum at a pH around 7.0. At pH values above 8.2-8.5 the effect was seen to diminish and practically disappear at pH 9.9, since no difference in freeness was found between samples with and without

TABLE VI

THE EFFECT OF ALUM CONCENTRATION AND pH OF ALUM ADDITION[1] ON THE S.-R. FREENESS OF AN UNBEATEN LOW-D.S. (0.035) CMC PULP

a) Effect of Alum Concentration: (pH constant)

pH of Slurry	Alum Concentration, (moles/liter) x 10^{-5}	S.-R. Freeness-20°C., cc.
7.0	no alum	550
7.0	1.1	458
7.0	1.5	440
7.0	2.2	455
7.0	3.0	580

b) Effect of pH: (alum concentration constant)

	7.0	no alum	550
	7.0	1.5	440
$(I)^2$	8.2	1.5	440
	8.5	1.5	467
	9.9	1.5	560
	7.0	no alum	600
	3.9	no alum	700
$(II)^2$	3.9	1.5	705
	4.5	no alum	655
	4.5	1.5	580

1 pH of the freeness sample was adjusted with dilute sulfuric acid (or NaOH). The appropriate amount of aluminum sulfate solution was added, the slurry was thoroughly mixed before the S.-R. freeness was determined.

2 There was a time lapse of about 5 days between correction of data for $(I)^2$ and $(II)^2$. This may perhaps be responsible for the different freeness values at pH 7.0 and no alum.

the addition of alum. Similarly, there appeared to be no effect of the alum at pH 3.9. It would seem therefore, that the effect of alum at the very low concentrations is limited to the approximate pH range 4.5 - 8.5 for the low-D.S. CMC pulps in suspension.

Concentration Versus the Amount of Alum in the Pulp Suspensions

To determine whether it is the concentration or the amount of alum which is the dominant factor in the effect at very low concentrations, neutral extractions of a low-D.S. CMC pulp were carried out in the presence of alum. The low-D.S. (0.035) CMC pulp was the same as was used in collecting the data for Table VI. An alum concentration of 1.5×10^{-5} moles per liter was found above to produce a minimum in freeness for this particular unbeaten pulp. The freeness sample under the above conditions consisted of 2.0 grams of CMC pulp suspended in one liter of water containing 1.5×10^{-5} moles of alum. When the same amount of the pulp was suspended in 200 ml. of water, then extraction at the same concentration and amount of alum, respectively, gave the results presented in Table VII. The procedure for the extraction of CMC pulps and isolation of the extracted material has already been described. The data makes it clear that the concentration rather than the amount of alum in solution is responsible for the above effect.

TABLE VII

EFFECT OF ALUM CONCENTRATION ON EXTRACTION OF CMC PULP (D.S. 0.035)

Alum Concentration,[1] moles/liter	Extracted Material, % ovendry pulp
1.5×10^{-5}	2.40
	2.70
7.5×10^{-5}	0.98
	0.98

[1] Alum concentration for minimum freeness: 1.5×10^{-5} moles/liter

It is obvious from the above that, while aluminum sulfate in very low concentrations solubilizes the CMC colloid, in relatively higher concentrations it acts as a coagulant. An investigation of this apparent reversal would be outside the scope of this study, but the literature reveals some interesting aspects which are tentatively presented in Appendix II.

HANDSHEET STRENGTH INCREASE IN LOW-D.S. CMC PULPS

Walecka (5) reports appreciably increased strength properties for handsheets formed from low-D.S. carboxymethylated rag pulps, as compared to those from the untreated fibers. Such increases in handsheet strength can be analyzed for contributing factors as described by Leech (24), in his investigations of the reasons for sheet strength increase when beater

adhesives are used. Since absolute measures of each factor were rather difficult to attain, he used methods of testing which gave satisfactory estimates. The following tests were utilized by Leech:

(1) Zero-span tensile strength for the strength of fibers.

(2) VVP bonding strength for the strength of bonds.

(3) Optical bonded area for the number of bonds.

(4) The Thwing formation for the distribution of fibers and bonds.

Supplementary information was obtained for Mullen bursting strength, Elmendorf tearing strength, and tensile-strength tests made on the sheets. The advantages and the distinct limitations of the tests involved have been discussed in detail by Leech (24). The one salient point which needs to be emphasized is that these tests are to be considered only as satisfactory estimates of the properties under consideration rather than as absolute measures.

THE STRENGTH OF FIBERS

Leech used the zero-span tensile test for estimating the strength of the fibers, realizing that the test is affected by bonding in the paper sheet. If the pulps are only lightly beaten, however, the effect of bonding is minimized for the purposes of any comparison of zero-span tensile strength values.

Walecka (5) measured the zero-span tensile strength of various low-D.S. CMC fibers, and found that increased values are obtained with

increasing degree of substitution on rag pulp. This led him to conclude that low-D.S. carboxymethylation may result in increased fiber strength. Such a conclusion, however, would be surprising in view of relevant information available in the literature. Single fiber tensile strength determinations with carboxymethylated (26), and acetylated fibers (1), show little change even at relatively high degrees of substitution. As such, Walecka's results with low-D.S. CMC pulps appear anomalous and single fiber tensile strength determinations were undertaken in the present study for CMC pulps at different degrees of substitution.

The IPC load-elongation tester, available in the Physics Department of the Institute, was used for determining the average breaking loads for single fibers (40). This instrument uses a cantilever supported at one end as a force sensing device, and the force in grams required to break a single fiber is automatically recorded by means of a recorder coupled to the instrument. The instrument is calibrated frequently with analytical weights.

In the main, the procedure developed at the Institute was followed (41). The various pulps made by Walecka were used in order to facilitate comparison with the zero-span tensile strength results already obtained by him. Approximately 1 gram of pulp was taken in each instance and soaked in a liter of distilled water overnight. The pulp was dispersed in a British disintegrator, and a small sample of the suspension was then withdrawn and diluted to obtain approximately 20 individual fibers

per milliliter of the slurry. A small representative sample of the slurry was poured into a shallow cavity in a Lucite dish placed on a microscope table. Single fibers were then picked out by means of dissecting needles under a binocular microscope. The fibers were mounted on small paper tabs, as is shown in Figure 7. The tabs were cut from the black paper ordinarily used as inner sheets in packaging photographic printing paper. The fiber was mounted nearly perpendicular to the slit in the tab and the fiber ends were then secured by means of a mounting cement consisting of a 20% solution of Vinylite AYAT (99.5 parts) and tributyl citrate (0.5 parts) in an alcohol-benzene (1:4) vehicle. The cement was allowed to dry for five days before testing.

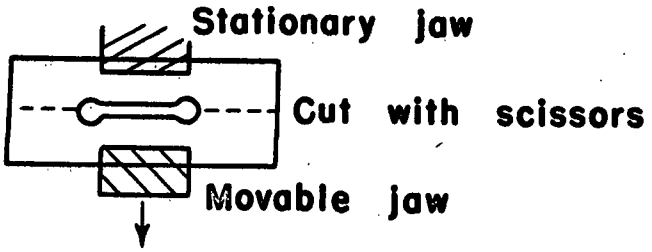

Figure 7. Paper Tab for Fiber Mounting

The two holes in the tab are punched with a paper punch, and the connecting slit, about 2-mm. wide, is cut with scissors prior to mounting

of the fiber. The ends of the slit are cut carefully with scissors after the mounted tab is fixed in the jaws of the tester. Table VIII gives the breaking load in grams for the various fibers, as averages of approximately 25 readings in each instance.

TABLE VIII

FIBER-BREAKING LOADS FOR CARBOXYMETHYLATED RAG PULPS

Pulp	Breaking Load, grams	Standard Deviations
Untreated, uncut	6.5	4.0
Untreated, cut[1]	7.6	3.2
Untreated, cut, solvent exchanged	7.3	3.4
Treated, cut, solvent exchanged	6.1	2.6
D.S. 0.006	5.9	2.0
D.S. 0.014	6.7	3.3
D.S. 0.022	6.2	2.5
D.S. 0.036	6.6	2.2
D.S. 0.048	5.8	3.2
D.S. 0.053	6.0	2.9
D.S. 0.062	6.5	2.7
D.S. 0.048, "acid form"	5.5	2.4
D.S. 0.048, "sodium salt form"	5.8	3.2

[1] Pulp beaten at 0.3% consistency. Refer p. 16-17

It is clear from the data above that the breaking load of single fibers is apparently independent of the degree of substitution, at least for the range of D.S. investigated. Furthermore, no recognizable difference in breaking strength is found even between the sodium salt form and the "acid" form of the CMC pulps. In view of the above, it is apparent

that Walecka's zero-span tensile strength data for the same pulps should not be interpreted in terms of changed individual fiber strength. More likely, the changes in zero-span tensile strength for the pulps probably indicate some interfiber bond breakage in the test. Such increases in zero-span tensile strength have been obtained by adding hydrophilic gums and beater adhesives to pulps, a case in which changes in individual fiber strength are rather improbable (24).

SHEET STRENGTH PROPERTIES

The remaining factors in the analysis, the strength of bonds, the number of bonds, and the distribution, are all concerned with sheet properties. We know from Walecka's work (5), however, that increased sheet strength is obtained with increasing substitution in low-D.S. CMC pulps. More significant was the finding that the strength increase was greatest if the CMC was in the sodium salt form. Even partial acidification with acetic acid resulted in appreciable loss of strength. To determine whether the effect is specific to acetic acid or if the loss in strength can be obtained by acidification in general, it was decided to study the effect of pH on sheet strength of CMC pulps, using mineral acid for acidification.

In the attempts made to determine the effect of pH, it was found that only a limited range of pH could be investigated. Decreasing pH values, below about 4.5, resulted in such an intense flocculation of the CMC pulps that no sheet formation was possible. Table IX, however,

shows the sheet properties of a CMC pulp (D.S. 0.035) at pH values 4.9, 7.0, and 10.0. The pulp was originally in the sodium salt form and the pH was adjusted in the sheet mold, just prior to drainage, with dilute sulfuric acid or sodium hydroxide. The handsheets were made in a British sheet mold using Institute Method 411.

Table X shows the effect of pH on sheet properties of the CMC pulp at different beating intervals. The pulp was beaten in a Jokro mill for the specified time intervals, and sheet pH was adjusted in the sheet mold. The same batch of beaten pulp was used for the sheets formed at different pH values for each beating interval. The Institute Methods were used for all the tests indicated.

The data in Tables IX and X make it obvious that the low-D.S. CMC pulp displays a maximum increase in strength at pH 7.0 and above. Sheets formed at pH 4.5 show consistently lower strength properties at all beating intervals. The markedly poorer formation is also evident at the acidic pH value. Table IX also gives the strength properties of the unbeaten, unsubstituted control pulp for comparison.

The strength properties of sheets formed at pH 4.5 from low-D.S. CMC pulps are found to be lower than those formed at alkaline or neutral pH values. This is true when acidification is effected either with acetic acid or sulfuric acid. As has already been mentioned, the CMC is only partially neutralized at this pH. To obtain the free acid form, lower

TABLE IX

EFFECT OF pH ON HANDSHEET PROPERTIES OF UNBEATEN CMC PULP (D.S. 0.035)

Pulp	pH	Basis Weight, pounds 25 x 40 x 500	Apparent Density	Mullen Burst, pt./100 lb.	Tear Factor, g./lb.	Tensile, lb./in.	Opacity, %	Thwing Formation Number
Treated control	--	45.6	9.12	35.1	3.31	8.80	82.0	24.9
CMC, D.S. 0.035								
	4.5	46.1	10.2	53.5	3.12	12.4	81.4	22.3
	7.0	46.0	10.7	62.6	3.17	13.9	77.7	44.0
	10.0	45.9	10.4	65.4	3.08	14.3	77.3	41.5

TABLE X

EFFECT OF pH ON HANDSHEET PROPERTIES AT DIFFERENT BEATING INTERVALS
(CMC Pulp D.S. 0.035)

Sheet Property	pH	Time of Beating in Jokro Mill, minutes 0	4	8	12	18	24
Basis weight, pounds 25 x 40 x 500	4.5	46.1	45.8	45.4	45.5	45.6	45.6
	7.0	46.0	45.7	46.0	45.8	45.3	46.1
	10.0	45.9	46.0	46.0	45.4	45.9	45.9
Apparent density	4.5	10.2	12.0	12.6	13.0	13.4	13.8
	7.0	10.7	12.1	12.8	13.4	13.7	14.4
	10.0	10.4	12.1	12.8	13.0	13.5	13.9
Mullen burst, points per 100 pounds	4.5	53.5	77.7	90.4	94.5	101.1	111.8
	7.0	62.6	87.3	103.9	110.7	116.3	117.6
	10.0	65.4	93.0	110.2	118.5	122.4	125.5
Tear factor, grams per pound	4.5	3.12	2.28	1.98	1.86	1.71	1.65
	7.0	3.17	2.28	2.02	1.88	1.76	1.63
	10.0	3.08	2.17	2.09	1.96	1.90	1.74
Tensile, pounds per inch	4.5	12.4	18.3	21.7	23.3	25.6	26.0
	7.0	13.9	20.9	25.2	26.6	27.2	29.1
	10.0	14.3	21.2	24.3	25.9	28.5	29.1
Tappi opacity, %	4.5	81.4	75.4	75.0	72.0	70.8	70.3
	7.0	77.7	73.4	70.9	70.7	68.5	68.7
	10.0	77.3	72.7	71.2	69.9	69.0	67.6
Thwing formation number	4.5	22.3	26.4	30.5	27.5	36.0	33.6
	7.0	44.0	43.4	49.2	55.1	50.0	44.3
	10.0	41.5	47.1	53.2	54.3	53.2	50.0

pH values have to be attained. No sheet formation is possible, however, if the CMC is acidified to the free acid form, because of intense fiber flocculation.

To obtain the sheet properties of the free acid form CMC pulps and to circumvent the experimental difficulties due to flocculation, it was decided to preform the sheet at pH 7.0 and then displace the liquid, in the wet sheet on the wire, with dilute acid solutions at the desired pH. This technique proved quite effective. It also enabled us to determine the effect of alum on sheet strength, by substituting dilute alum solutions as the displacing medium.

Using the sodium salt form of the CMC pulp and deionized water, a sheet was formed in the British sheet mold according to Institute Method 411. The sheet-machine container was tilted, and instead of couching, two sheets of filter paper were place carefully on the wet sheet. The container was once again fixed into position and the displacing dilute sulfuric acid or alum solution was poured gently on an inverted funnel hung just above the filter paper. Three 500-ml. batches of the solution were used in all. In each instance, the solution was allowed to drain slowly through the sheet. The container was again tilted, and after carefully removing the filter papers, the sheet was couched and further processed using Institute Method 411. Some of the physical strength properties of the handsheets obtained, are tabulated in Table XI. All the sheets were preconditioned to 73 $\pm$ 3°F. and 50 $\pm$ 2% relative humidity.

TABLE XI

STRENGTH PROPERTIES OF ALUM AND ACID-DISPLACED HANDSHEETS

Pulp D.S.	Displacing Solution[1]	Basis Weight, lb. 25x40x500	Apparent Density	Mullen Burst, pts./100 lb.	Tensile Strength, lb./in.	Opacity, %
Untreated control	--	45.9	9.12	35.1	8.8	82.7
Treated control	--	45.6	9.37	40.3	10.0	82.0
0.017	alkali	43.2	9.60	48.6	12.3	79.5
0.017	alum	45.9	8.74	37.7	9.6	81.0
0.017	acid	47.0	9.18	41.7	9.8	81.2
0.044	alkali	47.4	10.53	78.1	16.80	75.5
0.044	alum	44.9	9.16	39.0	9.6	81.2
0.044	acid	44.4	9.25	41.4	9.8	81.3

[1] The displacing solutions were made in distilled water with the following:

(1) Sodium hydroxide, pH 9.0 — "alakli".
(2) Aluminum sulfate, 0.001% — "alum". (1.5×10^{-3} moles per liter)
(3) Sulfuric acid, pH 3.5 — "acid".

All of the pulps considered above are unbeaten. It might also be mentioned that the Elmendorf tear factor was unchanged in all the instances above. The absence of any change in the tear factor was not surprising, since Walecka has shown that low-D.S. carboxymethylation does not influence the tear factor (5). One of the more obvious advantages of the technique of liquid displacement utilized above, is that strength comparisons can be made for the different conditions at the same formation.

Some very interesting conclusions emerge from Table XI. For instance, it is apparent that sheet strength increase, due to low-D.S. carboxymethylation, is only obtained if the CMC is in the sodium salt form. In the free acid form, or in the aluminum salt form, practically no increase is found over the untreated pulp. The effect of pH on sheet strength of CMC pulps, as was the case with freeness and filtration resistance values, was found to be reversible. The strength of the CMC sheet exposed to pH 3.5, could be regained, if the sheet was displaced once again with a dilute sodium hydroxide solution (pH 9.0).

The preceding suggests that the sheet strength properties of low-D.S. pulps could be controlled between a maximum of those of the sodium salt form and a minimum of the free acid form, the latter closely approximating the strength of the untreated rag pulp. This is evidently possible if the liquid displacement technique, described above, be used for adjustment of pH in sheet formation. The technique offers a number of obvious advantages. For instance, a single CMC pulp could be studied

to analyze the sheet strength variations in terms of the factors mentioned above. Extra variables, which would naturally be involved in working with a number of pulps of different D.S., would thus be eliminated. Need of further research here, however, is fairly obvious.

THE DISTRIBUTION OF BONDS (FORMATION)

Improvement in the formation of a sheet of paper is generally held to result in improved strength properties. Leech (24) claims that an appreciable portion of the strength increase, up to about 25%, obtained by addition of locust bean gum in pulps is due to improved formation. Mention has already been made of the visibly better dispersion of low-D.S. sodium CMC fibers in suspension. The sheets obtained from the sodium CMC pulps also show considerably improved formation as compared to those from the untreated rag pulp.

The data in Table XII give the effect of formation on the bursting strength of low-D.S. CMC pulp sheets. The sheets were made using the liquid displacement technique described above, and formation was measured on the Thwing formation tester (Institute Method 525).

The data in Table XII are for unbeaten pulps. The remarkable improvement of formation with carboxymethylation is obvious. The increase in bursting strength with substitution is also very apparent. The important consideration is, however, that by forming the sheets using the displacement technique and thereby holding the formation relatively constant,

virtually all the strength increase over the untreated rag pulp can be lost by acid displacement as well as displacement by alum solution. It would appear, therefore, that even though carboxymethylation results in very much improved sheet formation, yet formation, as such, could not have contributed appreciably to the resulting increase in strength.

TABLE XII

THE EFFECT OF FORMATION ON THE BURSTING STRENGTH OF CMC PULPS

	Sodium Salt Form		Acid Displaced (pH 3.5)	
Pulp D.S.	Thwing Formation Number	Mullen Burst, pts./100 lb.	Thwing Formation Number	Mullen Burst, pts./100 lb.
Untreated control	23.8	40.3	25.0	42.4
0.017	63.5	48.6	64.2	41.7
0.044	66.7	78.1	64.8	41.4

THE STRENGTH OF BONDS

The strength of the bonds was measured by the I.G.T. bonding strength tester (42). The quantity measured by the instrument is the strength of an aggregate of bonds and not the strength of individual bonds. Table XIII gives the bonding strength, in kilopoise-centimeters per second, of low-D.S. CMC pulps in the sodium salt form, after displacement with dilute acid, and after displacement with dilute alum solution. Using the liquid displacement technique, formation at each degree of sub-

stitution was held relatively constant. The Thwing formation and other sheet strength properties have already been presented in Tables XII and XI, respectively.

TABLE XIII

THE BONDING STRENGTH OF UNBEATEN CMC PULPS

Pulp D.S.	Bonding Strength, kilopoise-cm. per second (VVP) Sodium Salt	Acid Displaced (pH 3.5)	Alum Displaced
Untreated control	103	96	--
0.017	148	100	99
0.044	234	113	118

The data above make it pretty obvious that bonding strength, as expressed, is definitely involved in the strength increase due to carboxymethylation. For the sodium salt form of the unbeaten, low-D.S. CMC pulps, the bonding strength is found to rise with the degree of substitution. By displacement with acid or alum solution, practically all of the bonding strength increase due to substitution is lost. Table XI shows that under the same conditions all of the general sheet strength increase due to substitution is also lost. An increase in fiber bonding strength, therefore, appears to definitely contribute to the sheet strength increase due to carboxymethylation.

THE NUMBER OF BONDS (PER CENT RELATIVE BONDED AREA)

The optical method for determining bonded area was used as a measure

of the number of bonds. A modification of the procedure of Parsons (43) was used. The difference in the specific scattering coefficients of water-dried and unbonded butanol-formed pulp sheets is used as a measure of the relative bonded area. The unbonded sheets were produced by replacing the water in a sheet successively with acetone and butanol, so that the sheet is not dried from water but from a liquid with a low affinity for cellulose and hydroxyl groups. As is well-known, the method actually gives a measure of the area in optical contact. It is believed that the distances of separation of surfaces involved for optical contact and for bonding are of different orders of magnitude. The optical method, hence, can hardly be expected to measure the true bonded area, but it can, however, measure a quantity which is related to the bonded area.

The acetone-butanol handsheets were made with the control pulp. The other handsheets of the unbeaten CMC pulps were formed as has already been described. The General Electric Spectrophotometer (GERS) was used for measuring the reflectances. Using the Bureau of Standards opacity charts (44), the values of the scattering coefficients corresponding to R_o and R_∞ were determined. These were converted to the specific scattering coefficients by dividing by the basis weight expressed in grams per square centimeter. The difference in the specific scattering coefficients of the water-dried and the unbonded butanol sheet, divided by the specific scattering coefficient of the unbonded butanol sheet, then, gives the per cent relative bonded area. Table XIV gives the

per cent relative bonded area for the low-D.S. CMC pulp handsheets formed under the different conditions.

TABLE XIV

THE PER CENT RELATIVE BONDED AREA OF UNBEATEN CMC PULP SHEETS

Pulp D.S.	Relative Bonded Area, %		
	Sodium Salt	Acid Displaced (pH 3.5)	Alum Displaced
Untreated control	34.5	33.7	--
0.017	42.3	33.6	32.1
0.044	49.0	32.3	33.8

Thus we see, once again, that the increase in per cent relative bonded area, for the unbeaten pulps due to carboxymethylation, is almost completely lost if the CMC sheets are displaced with either acid or 1.5×10^{-3} M. alum solution. If we compare Tables XI and XIV, we find that the relative bonded area values closely follow the sheet strength pattern of the low-D.S. CMC pulps. Since the formation was held relatively constant by using the liquid displacement technique for sheet formation, the relative bonded area as a measure of the number of bonds is also established as a dominant factor in the strength increase due to sodium-carboxymethylation in rag pulp.

DISCUSSION OF RESULTS

The results in the preceding pages show clearly that the strength in rag pulps, due to carboxymethylation, occurred only when the low-D.S. CMC pulps were in the sodium salt form. If the wet sheets of the sodium salt form CMC pulps were displaced by a dilute mineral acid solution (pH 3.5) or a dilute (1.5×10^{-3} moles per liter) alum solution, the resulting strength of the sheets could hardly be distinguished from that of sheets formed from the untreated rag pulp or the treated control pulp. The acidified or alum-treated pulps were similar to the control pulps even in "feel" and appearance, and entirely lacked the slimy "hydrated" quality so characteristic of even the unbeaten sodium-carboxymethylated pulps. It is suggested that this behavior was probably due to the precipitation of the colloidally "dispersed" sodium-carboxymethylated cellulose on the fiber surface, since the acid form and the aluminum salt form carboxymethylcelluloses are insoluble in water. Moreover, the sodium CMC pulps were flocculated intensely in the presence of acid or alum. Even more significant, the colloidally dispersed relatively higher D.S. material, which could be extracted from low-D.S. sodium-CMC pulps under practically neutral conditions, was precipitated immediately by either acid or alum. Obviously, one cannot expect a swelling of the fibers in a precipitating medium.

Thus we see that almost the entire strength increase of low-substituted sodium CMC pulps could be lost by the rather simple process of acidification

or exposure to a dilute aluminum sulfate solution. Significantly enough, the handsheets obtained from CMC pulps of varying D.S. in the acid or the aluminum salt form showed physical strength properties very similar to those from the control pulps. Since the gain and loss in sheet strength during sodium-carboxymethylation and subsequent acidification were found to be practically equal, it is more than probable that the same factors are operative in each instance, except in an opposite direction.

Since the CMC pulps were highly flocculated in the presence of acid or alum, sheet formation was not possible directly. A liquid displacement technique, evolved by analogy from the "butanol-sheet" formation method, however, made sheet formation possible even under the above conditions. An additional advantage was obtained in that sheet formation could be held constant in order to provide a more sensible basis for comparison of sheet properties in the sodium salt, acid, or aluminum salt form low-D.S. CMC pulps.

An analysis of the sheet properties, in terms of the possible factors contributing to the changes in strength, revealed that:

1. The individual fiber strength was not significantly altered, since the individual fiber-breaking loads were found to remain unchanged through all the chemical modifications;

2. Even though the distribution of fibers in the sheets, as determined by the Thwing formation tester, was considerably improved due to

sodium-carboxymethylation, sheet formation as such could not have contributed appreciably to increased sheet strength. Virtually all of the sheet strength increase in low-D.S. CMC pulps could be lost if the fibers were exposed to acidic conditions even at the singularly improved, and constant, formation;

3. If the VVP test be taken as a measure of the bonding strength, it is obvious that an increased aggregate strength of bonds, if not the individual bonds, contributed to the sheet strength increase;

4. An increase in the number of bonds, as indicated by the relative bonded area values, similarly should definitely be considered as a contributing factor.

It is realized of course that the relationship between the fundamental property and the physical tests is not completely elucidated. However, since we are primarily concerned with relative changes in values, rather than the values themselves, the use of the tests is more defensible.

It is difficult if not impossible at this stage to further analyze the data and to attempt to relegate proportions to the two factors primarily responsible for the observed sheet strength increase. An intriguing observation of Walecka (5) may be resubmitted here. He found that the Elmendorf tear values of the sheets were not influenced to any appreciable extent by carboxymethylation. This was substantially corroborated in the present work. The decrease in tear factor of sheets due to beating of pulps is generally ascribed to increased interfiber bonding and to fiber-length reduction. With this in view, it might be suggested that the number

of bonds could not have increased very radically in sheets formed from sodium-CMC pulps. A possible conclusion therefore could be made that the dominant factor was an increased strength of bonds. This conclusion, however, is based almost entirely on deduction, and unless experimental verification is produced, it should be taken as such.

If we postulate improved hydrogen bonding in sheets made from low-D.S. CMC pulps, the difference in strength for the acid form and the sodium salt form can be easily explained. In the dispersed ("solubilized") sodium salt form, the CMC fibers are capable of much better interfiber contact and bonding than in the precipitated acid form. Any such improved bonding in the precipitated acid form would be possible only as intra-fiber bonding on the fiber surface rather than interfiber bonding. Thus, even though carboxyl groups are present in both instances, little improvement in sheet strength can be expected for low-D.S. CMC pulps in the free acid form since the precipitated CMC on the fiber surface has a very limited capacity to form any interfiber bonds. The above also gives indirect confirmation to the colloidal theory of beating and sheet strength development in general. Campbell's (51) "partial solubility" theory of beating appears to be particularly supported by observations made in this study.

CONCLUSIONS

1. Low-D.S. carboxymethylated rag pulps prepared by Walecka (5) displayed increased handsheet strength properties over the untreated fibers. It was shown in this study that the above strength increase is only found when the sodium salt form of the low-D.S. CMC pulps were used; when the acid or aluminum salt form of the derivative was used, no such strength increase occurred.

2. The literature reveals that while the alkali metal salts of higher D.S. carboxymethylcelluloses are soluble in water, most heavy metal salts, amphoteric multivalent metal salts, and the free acid form are insoluble in water. In reflecting these solubility characteristics, the well-dispersed low-D.S. sodium-CMC pulps in water flocculated markedly in the presence of the other ions. The "hydrated feel" of the unbeaten sodium-CMC pulps suspended in water, was lost in the presence of acid or alum.

3. Slightly alkaline water extractions of the unbeaten low-D.S. sodium-CMC pulps (by the procedure described) separated appreciable amounts of colloidally dispersed materials, which could be precipitated by dilute alum or acid solution. The isolated material displayed degrees of substitution approximately four to five times that of the low-D.S. CMC pulp from which it was extracted. Qualitative experiments with methylene blue showed that the material was probably extracted from the surface of the sodium salt form substituted fibers.

4. The action of dilute alkali appeared to be different from that of the extraction above. Even though 3% sodium hydroxide dissolved increasing amounts from the substituted pulps, very little material precipitated on acidification of the clear solution.

5. Acidification markedly increased the S.-R. freeness of low-D.S. sodium-CMC pulps. The increase in freeness was even sharper, when freeness of the pulps was measured in the presence of alum. At very low concentrations however, alum was found to decrease the freeness of the pulps, thus showing a reversal in action. It is suggested that, at very low concentrations, alum acts as a stabilizer for the colloidal system, while at higher concentrations it is a coagulating agent.

6. Analysis of filtration resistance data showed that sodium carboxymethylation apparently increased the effective specific volume and compressibility of the fibers. The calculated specific surface did not appear to be affected.

7. On the basis of single fiber breaking load determinations it was found that low-D.S. carboxymethylation did not noticeably affect the tensile strength of the fibers.

8. Comparison of handsheet properties of the sodium salt form and acid form of low-D.S. CMC pulps at similar formations (Thwing), showed that formation per se could not be a factor for the strength increase.

9. The increased values of VVP bonding strength and optically bonded area found for handsheets formed from low-D.S. sodium CMC pulps, could be reduced to those of the control pulps if the handsheets were treated with acid or alum. This indicates that both increased strength of bonds, and increased number of bonds might be involved in the handsheet strength increase of low-D.S. sodium CMC pulps.

SUMMARY

Investigations of low-D.S. CMC pulps prepared by Walecka (5) revealed that the sodium salt form displayed properties markedly different from those of the free acid form or the untreated pulp. In the sodium salt form, the CMC pulps show much better dispersion characteristics, lower freeness values, higher filtration resistances, and increased sheet strength values. In the free acid form the CMC pulps were highly flocculated. It is suggested that the difference in solubilities of the sodium salt form and the acid form CMC is responsible for the above behavior. The literature reveals that while the sodium salt of CMC is soluble in water, the free acid form is quite insoluble. Aluminum and other polyvalent metal ions, forming insoluble salts of CMC, also were found to flocculate the low-D.S. CMC pulps.

Low-D.S. CMC pulp handsheets were formed in the acid form, sodium salt form, and aluminum salt form by using a "liquid displacement" technique. It was found that all of the sheet strength improvement due to sodium carboxymethylation of the rag pulp could be lost if the CMC was converted to the free acid form or the aluminum salt form. Further analysis revealed that a greater number of bonds and improved bonding strength were contributing factors to the sheet strength increase in the sodium salt form of the low-D.S. CMC pulps. It is also shown that formation and individual fiber strength could not have contributed significantly to the improvement in sheet strength.

SUGGESTIONS FOR POSSIBLE FUTURE WORK

1. Studies on extraction of low-D.S. CMC pulps at pH 8.5, the nature of the extracted material, and a better method of D.S. determination of the extracted material.

2. Further investigation of the effect of metal ions, especially aluminum, on CMC pulps in suspension. It is suggested that electrokinetic studies be conducted on the various systems in order to approach the problem more fundamentally.

3. Studies on the strength of bonds involved in a sheet of paper, and direct experimental evidence for the suggested increase strength in bonding through carboxyl groups.

4. Investigation of the variables involved in the "liquid displacement" technique as evolved in this study.

5. Investigation of the filtration resistances of low-D.S. CMC pulps and analysis into components of specific surface, effective specific volume, and compressibility.

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APPENDIX I

Hydrogen bond formation presumably accounts for the well-known tendency to form molecular aggregates in compounds possessing hydroxyl groups. The classical case for such a compound is water, but the phenomenon is just as striking in alcohols and carboxylic acids. In vapors the hydroxyl compounds are generally found in the monomeric state, with the exception of carboxylic acids, while in the liquid state they associate through the hydroxyl groups (i.e., the hydrogen of one molecule attracts the oxygen of the next) and a chain formation takes place. It is, however, known from cryoscopic and vapor-pressure measurements that carboxylic acids are associated into dimers even in the gaseous state (45).

The study of the infrared spectrum of these substances provides particularly useful evidence for this interaction, since the -OH vibrations are in a region of the spectrum (approximately 3,600 $cm.^{-1}$) easily accessible to the observer, since they are comparatively independent of the structure of the compounds under investigation on account of the small mass of the hydrogen, and since they provide a direct measure of the forces involved. The infrared spectrum shows that the -OH frequency, which lies at about 3,700 $cm.^{-1}$ for gaseous substances, is shifted to 3,300 $cm.^{-1}$ in the liquid and at the same time greatly broadened. The half-widths change from about 40 $cm.^{-1}$ to about 600 $cm.^{-1}$. Cryoscopic measurements of hydroxyl compounds in solution indicate an increase in molecular weight.

The infrared spectra of dilute solutions of carboxylic acids are similar to those of alcohols; they consist of the sharp monomeric and the diffuse polymeric band, the latter being quite intense at a concentration (0.0005 moles per liter) for which it has completely disappeared from the alcoholic spectrum. This fact together with the large shift in the position of the association band shows that the forces producing association are much stronger in the acids than in alcohols or water (27). In alcohols the width of the association band is of the order of 300-350 cm.$^{-1}$, in acids it rises to 500-600 cm.$^{-1}$.

Tsubomura (28) presents infrared absorption data from which it is interesting to note that the intensity of the free hydroxyl bands of various compounds increases with their acidities. Since the shift of the frequency is generally taken as a good measure of the energy of the hydrogen bond, we may conclude that the intensity increases with the energy of the bond. This would seem to indicate that not only carboxyl-to-carboxyl but also carboxyl-to-hydroxyl would form appreciably stronger hydrogen bonds compared to bonds involving hydroxyl groups alone.

These conclusions, of necessity, are based on studies of low molecular weight compounds. Theoretically speaking, however, the conclusions should be of general validity and should cover the case in this study, if hydrogen bonding is considered to be involved in the strength of paper.

APPENDIX II

The complexity of the alum-in-water system is well recognized. In general, under acidic conditions (pH 4.0 or less), the trivalent aluminum ion is found to exist in solution, while under alkaline conditions (pH 9.0 and above), the ions exist as soluble alkali aluminates. In the medium pH range (pH 4.0 to 9.0) a number of aluminum hydroxide complexes, with varying solubilities, are held to exist in the system. It appears that the nature of these complexes is very much dependent on pH, concentration, and temperature. The structure of the complexes and the ionic equilibria involved are not entirely understood, but Ninck Blok (46) claims that alum hydrolyzes into aluminum hydroxides, sulfuric acid, and a number of intermediate products. There is a strong positively charged aluminum hydroxide complex which falls apart, at a pH value lower than 4.5, into aluminum ions. It is also known that a charge reversal of the complex takes place around pH 8.0, the charge being kept reversed above that pH (47).

In one of the earlier investigations, Kruyt (48) found that, in very small concentrations, potassium chloride, hydrochloric acid, and barium chloride increased the electrokinetic potential on glass, but quickly thereafter decreased it steadily though never discharging it entirely. Aluminum chloride, the only trivalent metal salt used, showed no indication of an increase of potential, but in very low concentrations (less than 0.0001 moles per liter), totally reversed the charge and maintained it reversed though approaching the value of zero at higher concentrations.

Such a charge reversal for aluminum ions at low concentrations has been confirmed in a number of instances and is taken as evidence by Tezak et al. (49) for the existence of tetravalent complex ions in the system. The latter are generally characterized by this behavior, and the charge reversal is presumed to constitute splitting of the tetravalent ions into divalent ions. More important, a number of instances have been recorded where, at these low concentrations, such ions act as stabilizers for negatively charged sols and as peptizing agents for negatively charged colloidal precipitates (50). Higher concentrations, of course, are found to coagulate colloidal systems, regardless of the electrolyte used.

The above considerations are especially relevant for low-D.S. CMC pulps. In the dispersed ("solubilized") sodium salt form, the presence of stabilizing low concentrations of aluminum ions disperses the fibers even more so. It is quite feasible that the aluminum ions act as cross links, presumably between the carboxyl groups. At higher concentrations of aluminum ions, precipitation of the CMC colloid on the fiber surface would naturally be expected to result in fiber flocculation. Confirmation for such a tentative hypothesis is provided by Swanson (52), who found that addition of very low concentrations of alum in sodium CMC solutions resulted in appreciably increased viscosity of the sodium CMC solution to below that of the initial value. Need of further research on the subject is quite obvious.